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THE

QUARTERLY JOURNAL

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I.—*On some Compounds of Urea, and on a New Method for the Determination of Chloride of Sodium and of Urea in Urine.*

By Justus Liebig.*

In the number of the Annals of Chemistry and Pharmacy for October, 1851, I have mentioned a compound of urea with protoxide of mercury, which is obtained in the form of a white gelatinous precipitate when a solution of protochloride of mercury (corrosive sublimate) is poured into a solution of urea, previously made alkaline by potassa.

Werther had already previously observed, that urea forms with protochloride of mercury a compound, crystallizing in flat prisms of a pearly lustre, which yields, according to Piria, a white precipitate with potassa, resembling the amide of mercury, and exploding when heated.

I have obtained three compounds of urea with protoxide of mercury; one of which is formed in a direct manner, and was described by Dessaignes a few weeks after the publication of my notice quoted above; the other two are obtained by precipitating an alkaline solution of urea with corrosive sublimate or nitrate of protoxide of mercury.

* The substance of this paper was communicated to the Society on the 10th of January, 1852 (*See* this Journal, Vol. V, p. 30).

A. Urea and Protoxide of Mercury, $2\,HgO + \overset{+}{U}$.*—On adding to a warm solution of urea protoxide of mercury suspended in water, the first portions are, as described by Dessaignes, completely dissolved in the liquor; an excess of protoxide of mercury is gradually changed into a white or yellowish-white powder. When dried *in vacuo*, the colour of this compound is slightly yellow; when heated in a tube, whilst dry, it is decomposed, without explosion; ammonia is given off, metallic mercury sublimes, and a yellow residue of mellon remains, which disappears only on ignition, when cyanogen gas is disengaged. In the moist state it decrepitates under the same circumstances; in the dark, sparks of a green light are observed.

By digesting protoxide of mercury in the water-bath with a solution of urea, I have in no instance succeeded in obtaining this compound entirely free from cyanate of protoxide or suboxide of mercury; a feeble, but very distinct disengagement of ammonia invariably takes place. The yellowish-white powder formed dissolves in this case, in hydrocyanic and hydrochloric acids, leaving a black residue of metallic mercury behind, and disengaging a small quantity of gas; the solution, when treated with milk of lime, gives off ammonia. This is the character of the cyanates. When digested in the water-bath for a longer period, the urea-compound loses its yellowish-white colour, and becomes lemon-coloured and granular. This latter compound exhibits the deportment of a basic cyanate of mercury.

2·000 grms., dissolved in hydrocyanic acid, gave on evaporation a dry residue of urea and cyanide of mercury weighing 2·394 grms., from which were obtained by precipitation with sulphuretted hydrogen 1·745 of sulphide of mercury, and by evaporation of the filtrate, 0·429 grm. of urea. This gives for

100 Urea and protoxide of mercury	Protoxide of mercury	81·09
	Urea	21·45
		102·54

The increase in weight, amounting to upwards of $2\frac{1}{2}$ per cent, appears to confirm the formula of Dessaignes, according to which 1 equiv. of water separates by the entrance of protoxide of mercury into this compound. The urea obtained by me was not however perfectly dry; it remained somewhat pasty, and possessed, feebly, the

* $\overset{+}{U}$ = 1 equiv. of urea.

reactions of sulphocyanide of ammonium. I am therefore not quite sure about the fact of water separating from the urea, inasmuch as in the silver-compound which contains 3 equivs. of oxide of silver, a similar replacement of water by oxide of silver does not occur.

By the same process of digesting a solution containing about 10 per cent of urea with protoxide of mercury until the reddish-yellow colour of the oxide was completely converted into a yellowish-white, I have, in several instances, obtained a urea-compound containing 3 equivs. of protoxide, instead of 2, just as the compound to be described forthwith.

B. Urea and Protoxide of Mercury, $3\,HgO + \overset{+}{U}$.—On adding solution of potassa to a solution of urea, and mixing with it a solution of corrosive sublimate, the liquid being continually kept alkaline by renewed addition of solution of potassa, a thick, gelatinous, snow-white precipitate is obtained, which, when brought into boiling water whilst still moist, after being first completely washed, is converted into a sandy, granular powder of yellow or yellowish-white colour. The water is hereby rendered alkaline, and takes up a certain amount of urea.

When dried, the powder is reddish-yellow; on being heated in a narrow glass tube, it is decomposed with decrepitation, and when moist, frequently with explosion; in the dark, the substance becomes luminous during this decomposition, and beautiful green sparks are observed; water and carbonate of ammonia are hereby given off, and metallic mercury sublimes, mostly without any residue of mellon; the compound dissolves in hydrocyanic and hydrochloric acids without effervescence; alkalies produce in the latter solution a yellowish-white precipitate.

The analysis of this compound from different preparations yielded the following results:

I. 4·606 grms. of substance, dried *in vacuo* over sulphuric acid, gave 4·152 of sulphide of mercury.

II. 2·685 grms. of substance, dried *in vacuo* over sulphuric acid, gave 2·436 of sulphide of mercury.

III. 2·1904 grms. of substance, dried *in vacuo* over sulphuric acid, gave 1·9605 of sulphide of mercury.

IV. 1·7578 grms. of substance, dried *in vacuo* over sulphuric acid, gave 1·5815 of sulphide of mercury.

V. 1·000 grms. of substance, by combustion with oxide of copper, gave 0·1144 of carbonic acid and 0·0594 of water.

VI. 2·094 grms. yielded by direct determination 0·350 grms. of urea.

Composition in 100 parts:

	Calculated.		I.	II.	III.	IV.	V.	VI.
Protoxide of mercury . .	324	84·37	84·1	84·3	83·91	84	—	—
Urea	60	15·63					15·6	16·6
	384	100·00						

C. Urea and Protoxide of Mercury, $4\,HgO + \overset{+}{U}$.—On precipitating a solution of nitrate of protoxide of mercury, instead of a solution of corrosive sublimate, with an alkaline solution of urea, a white, somewhat less gelatinous precipitate is obtained, which also loses this state in boiling water, and becomes a sandy powder. No distinct crystalline structure was observed under the microscope in either of these compounds.

The properties of this compound do not differ from those of the others previously described; it contains, however, more protoxide of mercury. The substance from different preparations, dried over sulphuric acid, yielded by analysis the following results:

I. 0·987 grms. gave 0·932 = 94·4 per cent. of sulphide of mercury.

II. 2·200 grms. gave 2·085 = 94·3 per cent of sulphide of mercury and 0·279 = 12·7 per cent of urea.

III. 3·000 grms. gave 2·860 of sulphide of mercury = 95·3 per cent and 0·329 = 10·96 of urea.

IV. 2·000 grms. gave 1·880 = 94 per cent of sulphide of mercury; these numbers correspond to the following composition:

	Calculated.		Found.			
			I.	II.	III.	IV.
4 equivs. of protoxide of mercury . .	432	87·804	87·82	87·3	88·72	87·4
1 „ of urea	60	12·196	—	12·7	10·96	—
	492	100·000		100·0		

Urea and Protoxide of Silver.—When freshly precipitated oxide of silver in the moist state is put into a solution of urea, and the liquid left in a warm place of from 40° to 50°, the oxide of silver changes its colour after one or two hours, appears to swell up from one point, and becomes granular and of a lighter grey colour; when the mass has assumed a uniform colour, and some of it is examined under the microscope, the powder is found to consist of transparent, pretty regular, scarcely coloured, prismatic crystals. The compound is readily soluble in nitric acid without disengagement of gas, but with

difficulty in ammonia; when touched at one point with an ignited body, it undergoes a tinderlike combustion, a large quantity of ammonia being disengaged, and is converted into a darker coloured coherent mass, which now effervesces with acids and evolves with nitric acid, besides carbonic acid, nitric oxide, or nitrous acid. On heating the burned mass in a tube, a strong smell of cyanic acid is perceived, and a white body sublimes possessing the properties of cyamelide. The urea-compound is converted by the first combustion into a mixture of metallic silver and cyanate of suboxide of silver. On being heated in a tube, a second incandescence takes place; the cyanate of suboxide of silver is decomposed; part of the cyanogen escapes in form of cyanic acid; and another portion remains with the silver; in fact, when the residue is boiled with dilute nitric acid, a mixture of white cyanide of silver and brown paracyanide of silver is left behind.

By analysing the compound, from different preparations, there was obtained:

I. From 2·0340 grms. of urea-oxide of silver, dried *in vacuo* over sulphuric acid, 0·2960 grms. of pure urea = 14·25 per cent.

II. From 1·052 of the compound 0·826 of metallic silver.

III.	„	1·585	„	„	1·248	„	„
IV.	„	1·547	„	„	1·222	„	„
V.	„	1·758	„	„	1·385	„	„
VI.	„	1·939	„	„	1·529	„	„
VII.	„	1·574	„	„	1·242	„	„

These results lead to the following composition:

	Calculated.		I.	II.	III.	IV.	V.	VI.	VII.
3 eqs. of oxide of silver	348	85·29	—	84 32	84·54	84·81	83·50	84·68	84·75
1 eq. of urea . . .	60	14·71	14·25	—	—	—	—	—	—
	408	100·00							

Nitrate of Urea and Protoxide of Mercury.—On adding a solution of nitrate of protoxide of mercury to a solution of urea, a snow-white, flocculent precipitate is immediately formed, containing urea, protoxide of mercury and nitric acid. According to the proportion in which the two solutions are mixed, or according to the amount of acid in the mercury-salt, three compounds or mixtures of them are formed, differing by their amount of protoxide of mercury.

These various compounds possess the following properties in common: they yield, when burned with oxide of copper, a mixture of gases containing nitrogen and carbonic acid, in the proportion of

3 to 2 volumes; this is the same proportion as that in nitrate of urea. On removing the protoxide of mercury by means of sulphuretted hydrogen, pure nitrate of urea remains in the liquor filtered off, which crystallizes to the last drop. These compounds differ, therefore, only by their unequal amount of protoxide of mercury; they dissolve in hydrocyanic and hot nitric acid without leaving a residue: potassa produces a white precipitate in the nitric solution. Heated for some time, when dry, in a current of warm air, decomposition ensues; they assume a yellowish colour, and their nitric solution yields now a yellowish precipitate with potassa.

A. $NO_5, \overset{+}{U} + 4\,HgO$.—When the solution of urea is mixed with the mercurial solution in a *very dilute* and warm state, and the precipitate formed is digested with the liquor, it quickly aggregates to a heavy white powder, which presents under the microscope the form of roundish grains, consisting of very small, concentrically grouped needles. In the dry state this powder rolls on paper like fine sand. After being dried *in vacuo*, there was obtained by solution in hydrocyanic acid and precipitation with sulphuretted hydrogen from:

I. 1·990 grms. of the substance, 1·680 sulphide of mercury = 88·4 per cent.

II. 2·000 grms. of the substance, 1·700 sulphide of mercury = 85· per cent.

III. 2·000 gave, after the removal of the mercury, 0·410 of nitrate of urea, and after its saturation with carbonate of baryta 0·681 nitrate of baryta and urea. On treating this 0·681 grm. with alcohol, 0·462 of nitrate of baryta was left.

This compound accordingly consists of:

	Calculated.		I.	II.	III.
1 equiv. nitric acid	54	9·90	—	—	9·55
1 „ urea.	60	10·98	—	—	10·95
4 „ protoxide of mercury	432	79·12	78·58	79·14	—
	546	100·00			

B. $NO_5, \overset{+}{U} + 2\,HgO$.—On adding a solution of crystallized nitrate of urea to a moderately dilute solution of nitrate of protoxide of mercury, mixed with some nitric acid, until a slight cloudiness ensues which does not disappear again, then filtering and allowing the mixture to stand quietly, solid hard crystalline crusts are deposited over night, consisting of an aggregate of small, rectangular, brilliant,

transparent tablets. By treatment with boiling water, these crystals are decomposed; they become dim and opaque, and are transformed into the compound just described, the water removing from them nitrate of urea. The analysis yielded the following results:

I. 2·400 grms. gave 1·696 sulphide of mercury.
II. 2·000 „ „ 1·414 „ „ „
III. 2·000 „ „ 0·700 grm. nitrate of urea, from which were obtained 0·780 nitrate of baryta.

This compound therefore consists of:

	Calculated.		I.	II.	III.
1 equiv. nitric acid	54	16·37	—	—	16·1
1 „ urea	60	18·18	—	—	18·9
2 „ protoxide of mercury .	216	65·45	65·6	65·7	—
	330	100·00			

C. $NO_5, \overset{+}{U} + 3\,HgO$.—On adding a dilute solution of nitrate of protoxide of mercury to a solution of urea, as long as a precipitate is formed, and allowing the white mass to stand in a warm place of from 40° to 50°, the precipitate is converted into six-sided transparent tablets, amongst which are observed under the microscope, roundish grains of the first, and isolated square tablets of the second compound. In no instance have I succeeded in obtaining this compound quite pure and free from those admixtures; the microscope however plainly indicates that we have before us a compound totally different from the other two.

2·000 grms. gave 1·550 sulphide of mercury, 0·864 nitrate of baryta and urea, and from this 0·597 nitrate of baryta.

3·000 grms. gave 2·488 sulphide of mercury, 1·256 nitrate of baryta and urea, and 0 836 nitrate of baryta.

The first analysis yields for 100 substance, 77·5 sulphide of mercury; the second, 80·3. Assuming the compound to contain 3 equivs. of protoxide of mercury for 1 equiv. of nitrate of urea, 79·4 per cent of sulphide of mercury should be obtained from it, when in a pure state.

QUANTITATIVE DETERMINATION OF CHLORINE IN NEUTRAL LIQUIDS BY MEANS OF PROTOXIDE OF MERCURY.

Nitrate of protoxide of mercury added to a solution of urea, immediately produces a thick white precipitate; this precipitation does not take place with solution of corrosive sublimate.

On mixing a chlorine-compound of the alkali-metals with nitrate of

protoxide of mercury, a mutual transposition into sublimate and nitrate of the alkaline base takes place. A saturated solution of chloride of sodium, mixed with a concentrated solution of nitrate of protoxide of mercury, solidifies into a foliated mass of crystals of protochloride of mercury.

On mixing a solution of urea with chloride of sodium, and adding gradually, in small portions, a dilute solution of nitrate of protoxide of mercury, a white cloudiness ensues at the place where both liquids meet, disappearing, however, immediately on shaking, leaving the liquor as bright and transparent as before; without the chloride of sodium, it would have retained its cloudiness. This deportment lasts until the nitrate of protoxide of mercury added, exactly suffices to transform the chloride of sodium into corrosive sublimate; beyond this limit, a single drop of the mercurial salt produces a lasting white cloudiness.

From this deportment it is evident that, if we know the amount of mercury in the solution of nitrate of protoxide of mercury which has been added to a solution of urea, containing an unknown quantity of chloride of sodium, until a permanent precipitate is formed, we also know the amount of chlorine or of chloride of sodium in this solution; 1 equiv. of mercury in the mercurial solution used, corresponds exactly to 1 equiv. of chlorine (or chloride of sodium).

If, on the contrary, the amount of chloride of sodium in the solution of urea be known, and the amount of mercury in the mercurial solution be unknown, the latter amount may be calculated with facility.

This method of determining the amount of chloride of sodium is particularly applicable in the case of urine, inasmuch as no urea requires to be added; as a matter of course, it may also be used with advantage for the estimation of the chlorine in brine or sea-water, and, generally speaking, in every case when a large number of such determinations are to be made in the shortest possible time. In those cases in which the chloride of sodium is not to be estimated in urine, but in other neutral liquids, the method, now to be described, has to be modified in some points.

Preparation of the Nitrate of Protoxide of Mercury.—If chemically pure mercury be at our disposal, this preparation does not offer any difficulty. 5 parts of nitric acid of 1·425 spec. grav. are poured on 1 part of mercury in a beaker; this is then placed over a water-bath, and heated, with frequent additions of a few drops of nitric acid, until no more red vapours escape, and a drop of it mixed with solution of chloride of sodium ceases to produce a cloudi-

ness; the solution is then evaporated in the same vessel, and over the water-bath, to the consistence of a syrup. The mercury of commerce cannot be used for this purpose, because it always contains lead and bismuth, which render the determination of chlorine uncertain. The presence of lead or bismuth immediately produces a white cloudiness, or an opalescence, on mixing the mercurial solution with a solution of chloride of sodium containing urea, which renders it difficult to recognise clearly the limit—or the point when the urea-compound of the nitrate of protoxide of mercury is precipitated. It becomes, therefore, necessary first to obtain a crystallization of nitrate of suboxide of mercury by boiling dilute nitric acid with an excess of metallic mercury, concentrating and cooling. The crystals of this salt are then separated from the mother-liquor containing the other metals, washed first with some dilute nitric acid and then with water, whereby part of the salt may be transformed into a basic salt; they are next dissolved in nitric acid, and heated until no further escape of nitric acid takes place, and a drop of it tested by chloride of sodium is no longer precipitated. The solution of the salt of the protoxide is now evaporated in a water-bath, to the consistence of a syrup, and diluted with 10 times its bulk of water. Should there be, after 24 hours, a separation of basic salt of the protoxide from the mixture, it must be filtered off.

In order to employ this mercurial solution for the determination of chloride of sodium, it must be graduated—that is to say, reduced to a definite amount of protoxide. This may be effected in two ways: it is either graduated in a direct manner with a solution of pure chloride of sodium of a definite strength; or the amount of protoxide of mercury is estimated, and the solution then diluted with such a quantity of water, that a cubic centimeter of the dilute solution indicates exactly 10 milligrammes of chloride of sodium. Both methods require a solution of chloride of sodium of a definite strength.

When pure transparent rock-salt, in coarse pieces, is digested with water during twenty-four hours, at a temperature of from 12° to 24°, and the liquor frequently shaken during that time, an unvarying quantity of the salt is dissolved.

10 cub. cent. of the clear filtered solution contain a definite, invariable weight of chloride of sodium; a determination by the balance is hereby not required.

100 parts of water dissolve, according to the experiments of Fuchs, 36; according to the latest investigations of Fehling, 35·91; and

10 parts by weight of the solution contain 2·6423 of chloride of sodium. The spec. grav. of the solution is, according to Karsten, 1·2046; according to Anthon, 1·205; 10 cub. cent. of a saturated solution should consequently contain 3·183 grms. of chloride of sodium.

By evaporating 10 cub. cent. of saturated solution of chloride of sodium, I have obtained 3·185, 3·184, 3·195, 3·175, mean 3·184 grms. of chloride of sodium. This is the number obtained by Fuchs and Fehling.

If, therefore, 20 cub. cent. of solution of chloride of sodium, saturated at the ordinary temperature, be exactly measured by means of a pipette (the drop adhering to the end of the pipette not blown off), and mixed with 298·4 cub. cent. of water, we have:

298·4 cub. cent. of water
20·0 „ „ solution of chloride of sodium } 318·4 cub. cent.

of dilute solution of chloride of sodium containing 2 × 3184 milligrammes of this salt. 10 cub. cent. of this solution contain, therefore, 200 milligrammes of chloride of sodium.

Preparation of the test-liquor for the determination of Chloride of Sodium.—In a small pipette, holding exactly 10 cub. cent. of liquor when filled to a certain line in the narrow tube, 10 cub. cent. of the solution of chloride of sodium, just described, are measured off, and put into a small beaker; to this are added 3 cub. cent. of a solution of urea, containing in 100 cub. cent. 4 grms. or in 1 cub. cent. 40 milligrammes of urea.*

The dilute solution of mercury, to be graduated, is now put into a burette, the height of the liquor noted, and added drop by drop to the solution of chloride of sodium mixed with urea, whilst the liquor is kept in a rotatory motion. The test is finished as soon as a distinct precipitate is permanently formed in the liquor.†

If for 10 cub. cent. of solution of chloride of sodium 7·8 cub. cent. of the mercurial solution have been required to induce the precipitate, the latter is too concentrated to admit of an exact graduation;

* For the purpose of measuring this solution, a small measure is made of a narrow test-tube, in which 3 cub. cent. of liquor are measured off; the height of the liquor is marked by a scratch with a file; a few drops more or less are of no consequence.

† An opalescence of the liquor is not to be regarded; it is caused by a trace of foreign metals; it may immediately be recognised as not pertaining to the test, when, after its appearance, the cloudiness of the liquor is not increased by the addition of a few drops of the mercurial solution. This is not the case when the cloudiness has been caused by the urea-compound; every additional drop of the mercurial solution then produces a cloud, by which the liquor is rendered more opaque than it was before.

it has then to be diluted with its bulk of water, and the test to be made a second time. Suppose 15·5 cub. cent. of the mercurial solution have now been required to produce a cloudiness in 10 cub. cent. of the solution of chloride of sodium mixed with urea; then to 155 volumes of this mercurial solution, 45 volumes of water must be added, whereby 200 volumes of a solution are produced, of which 20 cub. cent. indicate exactly 200 milligrammes of chloride of sodium, or 1 cub. cent. 10 milligrammes.

If in the first trial 2·7 cub. cent. of mercurial solution be required for 10 cub. cent. of the solution of chloride of sodium, 5 or 6 times its bulk of water must be added before the first graduation is made. In short, the mercurial solution to be graduated should not be too far removed in concentration from the amount which it is ultimately to contain.

The correctness of the measurements is finally controlled by a special experiment; the degree of cloudiness, permanently obtained on mixing 20 cub. cent. of the test-liquor with 10 cub. cent. of the solution of common salt with urea, must be kept in view when making the real estimations. In these quantitative determinations of chloride of sodium, a source of error easily avoided, however, by a little practice, exists in using too much mercurial solution, whereby the cloudiness is increased, or too little, whereby it is diminished.

The test-liquor, the preparation of which I have just described, is calculated for those cases in which no other salts, besides chloride, and no excess of urea exist in the solution; it leads, however, to a slight error, when employed for determining the chloride of sodium in urine, inasmuch as it indicates a smaller amount in urine than really exists therein. This error is occasioned by the cloudiness, the index of the termination of the experiment, appearing somewhat earlier in the presence of much urea and other salts than without, inasmuch as the precipitate is less soluble in such liquids. A deposit of nitrate of urea and protoxide of mercury is, as a matter of course, not produced until the liquor is saturated with it; the mercurial solution always contains free nitric acid, which dissolves more of it than water, and this again more than a nitric solution of urea.

Since then urine generally contains more urea than has been added to the solution of chloride of sodium when graduating the mercurial solution, and this urea seizes part of the free nitric acid of the mercurial salt, forming nitrate of urea, the solvent power of the liquor for the precipitate is diminished, and the precipitate appears somewhat sooner—that is, somewhat less of the test-liquor is required to produce the cloudiness. This error is completely obviated by adding

5 cub. cent. of a cold saturated solution of sulphate of soda to the 10 cub. cent. of solution of chloride of sodium, mixed with 3 cub. cent. of solution of urea, and then graduating the test-liquor.

Nitrate of protoxide of mercury produces, with a solution of sulphate of soda, a yellow pulverulent precipitate of *turpethum minerale*. If the sulphate of soda contains chloride of sodium, the precipitate of turpethum, on addition of nitrate of protoxide of mercury, is not formed until the chloride of sodium is converted into sublimate; the addition of sulphate of soda alters, therefore, the experiment only in this manner, that the free acid of the mercurial salt combines with the sulphate of soda to form an acid salt, whereby the same effect is produced as by an excess of urea.

On adding urea and then nitrate of protoxide of mercury to a solution of sulphate of soda, free from chloride of sodium, the liquor coagulates, even when tolerably dilute, to a gelatinous mass of a snow-white compound, containing sulphuric acid, urea, and protoxide of mercury; it is somewhat less soluble in water and sulphuric acid than the corresponding nitrate.

The method of determining chlorine by means of a silver-salt is so exact that no more exact process could be said to exist; but the method of estimation with nitrate of protoxide of mercury, just described, is not inferior to that with nitrate of silver, as regards precision; it is applicable, however, only to neutral, or very slightly acid, or alkaline liquids, because an excess of acid prevents the precipitation of the urea-compound.

The following numbers enable us to make a comparison of both methods; they refer to very dilute solutions of chloride of sodium, presenting but very slight difference in the amount of chloride of sodium.

	Amount in 10 cub. cent. of the solution.		Estimated by nitrate of protoxide of mercury.
I.	81·5	milligrammes	81·6
II.	80·2	„	79·8
III.	82·7	„	82·3

We observe readily that these numbers do not differ from each other in a greater degree, than in the case of determinations made with standard solutions of nitrate of silver in the usual way.

The only advantage the nitrate of the protoxide of mercury has over the silver-salts consists, as I believe, in the circumstance, that the termination of the experiment is indicated by the commencement of the reaction. In using nitrate of silver the experiment is finished, when no farther precipitate is perceptible; in this case the cloudi-

ness of the liquor, the difficulty to render it clear in order to observe the end of the experiment, impedes the dispatch of the execution. In using the mercury-salt, some dozen analyses may be made in an hour; hence, this method is particularly applicable to technical purposes, for the estimation of chloride of sodium in Glauber's salt, and, after previous neutralization, in the soda of commerce.

In order to determine the chloride of sodium in urine, it is necessary to remove previously the phosphoric acid contained in it. I have found a mixture of 1 volume of a cold saturated solution of nitrate of baryta, and 2 volumes of cold saturated baryta-water, to answer this purpose very well. To 2 volumes of the urine to be examined, 1 volume of this mixture is added, and the precipitate formed filtered off; the liquor is alkaline from the excess of baryta; this alkaline reaction must be removed by means of nitric acid.

For the experiment, 15 cub. cent. of this liquor are taken, corresponding to 10 cub. cent. of urine; and for the measuring of it a small pipette is used, holding exactly this volume, when filled to the line, without subdivision. The liquor is put into a small beaker-glass (the last drop adhering to the pipette not blown or taken off), and mixed with the mercury-solution whilst it is continually being stirred. When cloudiness ensues, the quantity of test-liquor used is read off from the burette. Every cub. cent. used corresponds to 10 milligrammes of chloride of sodium.

By this method, I have made a large number of comparative experiments, with a solution of silver also graduated for 10 milligrammes of chloride of sodium in 1 cub. cent. of water; and the following numbers may furnish a specimen of the precision of the first, and of its close approximation to the ordinary method:

		By means of nitrate of: silver.	protoxide of mercury.	
		Milligrms.	Milligrms.	
1.	10 cub. cent. of morning urine contained	115·4	115·0	Chloride of sodium.
2.	10 „ „ „ „ „ of a child	110·	110·	
3.	10 „ „ of urine secreted after dinner	164·	164·	
4.	10 „ „ „ „ before dinner	189·	188·5	
5.	10 „ „ „ „ „ „	74·	74·	
6.	10 „ „ „ „ „ „	142·8	142·	
7.	10 „ „ „ „ after taking tea	127·5	127·5	
8.	10 „ „ „ „ „ „ beer	27·7	27·7	
9.	10 „ „ „ „ before bed-time, after taking beer	25·	25·	
10.	10 „ „ of the same urine	25·	25·	
11.	10 „ „ of urine (woman)	110·	110·	
12.	10 „ „ of the same urine	110·	110·	

The correctness and accordance of these determinations depends chiefly upon this point, that, in neutralizing the urine mixed with the baryta and nitrate of baryta, no more nitric acid is added than is just required in order to produce a feebly acid reaction. For this reason it is preferable to acidulate with nitric acid the whole filtrate, of which a small portion is kept back, and not the 15 cub. cent. measured off for the test; one drop too much is of no consequence in 100 or more cub. cent. of liquor, whilst if added to the small portion for the test, it would interfere with the precision of the experiment.

In determining urea in urine, the amount of chloride of sodium in it causes an error, which, for very accurate analyses, is obviated by previously removing the chlorine; and in this case the determination of the chloride of sodium, by means of nitrate of mercury, serves to indicate the exact amount of silver-solution graduated for the same quantity of chloride of sodium, which is to be added to the urine without further experimenting.

DETERMINATION OF PROTOXIDE OF MERCURY IN A SOLUTION OF NITRATE OF MERCURY.

On mixing solutions of nitrate of protoxide of mercury and phosphate of soda, a white flocculent precipitate of phosphate of protoxide of mercury is immediately formed, which, on being left in the liquor, rapidly becomes crystalline.

Solution of corrosive sublimate, however, may be mixed with the alkaline phosphate without producing a precipitate.

On adding solution of chloride of sodium to the mixture of the two former salts, before the precipitate becomes crystalline, the phosphate of protoxide of mercury formed immediately decomposes with the chloride of sodium, into sublimate and phosphate of soda; the precipitate formed disappears, and the liquor becomes clear and bright.

On this deportment I have based a method of determining the amount of protoxide of mercury in its nitric solution with tolerable precision. 1 equiv. of phosphate of protoxide of mercury requires to redissolve it 1 equiv. of chloride of sodium; if, therefore, the amount of chloride of sodium added be known, the amount of mercury in the mercurial solution is also known.

Since the equivalent of chloride of sodium is almost one half of that of protoxide of mercury, this method is not so precise and accurate as the determination of chloride of sodium by means of the mercury-salt; inasmuch as a small error in the addition of the solution of chloride of sodium causes one which is twice as great in

the calculation of the mercury. For certain purposes, however, especially for those which I have in view, this method is sufficiently exact.

Preparation of the normal solution of Chloride of Sodium to be employed for determining the Mercury.—According to the equivalents of chloride of sodium and of the protoxide of mercury, 108 protoxide of mercury correspond to 58·6 chloride of sodium, or 200 of oxide correspond to 108·52 of the salt.

If, therefore, 20 c. c. of a saturated solution of chloride of sodium be mixed with 566·8 c. c. of water, we have 586·8 c. c. of a dilute solution of chloride of sodium, containing in the whole 6368 milligrammes of chloride of sodium (viz. the amount contained in 20 cub. cent. of the saturated solution); in 10 cub. cent. there are, therefore, 108·52 milligrammes of chloride of sodium, corresponding to 200 milligrammes of protoxide of mercury (1 cub. cent. of solution of chloride of sodium =20 milligrammes of protoxide of mercury).

In order to determine with some accuracy the amount of oxide in a solution of nitrate of protoxide of mercury by means of this method, the solution should not be too concentrated, partly for the sake of measuring exactly, and partly on account of the limits of the reaction being more easily perceived in dilute liquors than in concentrated ones; it is desirable that the mercurial solution should not contain more than from 180 to 200 milligrammes of protoxide of mercury in 10 cub. cent.

In order to determine the concentration, the following preliminary experiment is made:—10 cub. cent. of the solution of chloride of sodium are mixed with 4 cub. cent. of a cold saturated solution of phosphate of soda (the officinal salt), and to this mixture the mercurial solution is poured from a burette, until, on shaking, the precipitate does not any longer disappear. Suppose 2·4 cub. cent. of mercurial solution had been used, they would then contain 200 milligrammes of oxide. This is too concentrated; 1 cub. cent. of it contains upwards of 80 milligrammes of oxide, but the exact determination requires that 1 cub. cent. should not contain more than 20 milligrammes. This solution should therefore be diluted with 3 volumes of water before the actual experiment is made.

Of this dilute solution of mercury, 10 cub. cent. are now put into a beaker, mixed with 4 cub. cent. of the above-mentioned solution of phosphate of soda, and the graduated solution of chloride of sodium added from the burette; the solution is kept in constant motion, and the test added very slowly towards the end, until the white precipitate formed is completely redissolved.

The addition of the solutions of phosphate of soda and of chloride of sodium must follow in rapid succession: if but a few minutes

elapse between the two additions, the phosphate of protoxide of mercury becomes crystalline, and does no longer dissolve, or at least with difficulty. Moreover, the solution of mercury must not contain too much free acid; it contains the proper amount, if, after the addition of the phosphate of soda, the mixture does not exhibit an acid reaction. If it has an acid reaction, it must previously be mixed with a few drops of carbonate of soda, until a basic salt is precipitated, which is redissolved by means of one or two drops of nitric acid.

It is a special character of this method that its errors depend chiefly on the circumstance of one or more drops of solution of chloride of sodium being added in excess, in order to redissolve the precipitate. The more chloride of sodium is used for a given volume of the solution of mercury to effect this end, the more oxide is supposed to be in this volume; the error in question increases, therefore, the amount of mercury found beyond the real amount. Since the phosphate of mercury is slightly soluble in the liquor, and since, finally, the solution of chloride of sodium is graduated with regard to this error, this discrepancy is generally very slight. If the method be reversed (viz., if the solution of mercury be poured into a mixture of the solutions of chloride of sodium and phosphate of soda) a slight excess of solution of mercury is always added, to make the precipitate appear, because it does not become permanent until the liquor is saturated with it. According to this mode of proceeding, therefore, the amount of mercury obtained is too low.

The determinations become still more exact, if both methods are combined in the following manner:

(Method I).—10 cub. cent. of the solution of mercury are poured into a beaker, 3 to 4 cub. cent. of a solution of phosphate of soda added, and then immediately, without waiting till the precipitate has become crystalline, the solution of chloride of sodium is added from the burette, until the precipitate has disappeared. Suppose 12·5 cub. cent. of solution of chloride of sodium had been used for this purpose, 12·5 cub. cent. of the same solution are then measured off.

(Method II).—3 to 4 cub. cent. of phosphate of soda added, and the same solution of mercury poured into this mixture from the burette, until a precipitate appears. Suppose 10·25 cub. cent. of the solution of mercury have been used for this purpose, then the true amount is as follows:

There have been used for:

I.	10	c. c.	of solution of mercury,		12·5	c. c.	of solution of chloride of sodium.
II.	10·25	c. c.	„	„	„	12·5	c. c.	„	„	„
	20·25					25·0				

Now, since every cub. cent. of solution of chloride of sodium corresponds to 20 milligrammes of protoxide of mercury, the 25 cub. cent. used indicate $20 \times 25 = 500$ milligrammes of protoxide of mercury which are contained in 20·25 cub. cent. of the solution of mercury.

The following experiments may serve as a critical illustration of this method:

a. 7·480 grms. of pure mercury, and 24 grms. of nitric acid of 1·402 spec. grav., were put into a beaker, and evaporated in a water-bath to the consistence of a syrup, then mixed with water so as to bring the volume of the liquor to 400 cub. cent. 10 cub. cent. of this solution contained, therefore, 187 milligrammes of mercury.

When tested according to method I. it was found to contain 190·8 milligrms.
And according to method II. . . . . 184·8 „

Mean . . . . . 187·8 „ of mercury.

b. 6·993 of mercury dissolved in nitric acid in the same manner, and diluted to 400 cub. cent; 10 cub. cent. contained 174·8 milligrammes of mercury:

Found according to the method I. · 177 milligrammes
„ „ „ „ II. . 172·4 „

Mean 174·7 „ of mercury.

c. 8·321 of mercury dissolved in the same manner, and diluted to 500 cub. cent.; 10 cub. cent. contained 166·4 milligrammes of mercury:

Found by the method I. . . 170·2 milligrammes
„ „ „ II. . . 163·4 „

Mean 166·8 „ of mercury.

d. From 10 cub. cent. of a solution of an unknown amount of oxide there was obtained by precipitation with potassa, 1·436 grms. of protoxide of mercury, and by the test-liquors in the mean, 1·446 grms.

e. 31·669 of mercury dissolved in nitric acid in the manner described above, and diluted with 443 cub. cent. of water; 10 cub. cent. contained 772 milligrammes of oxide. 1 volume of this solution was mixed with 3 volumes of water; 10 cub. cent. of this dilute liquor contained 193 milligrammes of oxide.

Found by the method	I. . .	192·5	milligrammes
„ „ „	II. . .	183·	„
	Mean	187·9	„ of oxide.

Instead of phosphate of soda, pyrophosphate of soda, neutral chromate of potassa, and other salts which do not precipitate corrosive sublimate, may be used.

As a matter of course, this method is only applicable to nitric solutions of mercury, containing no metals that are precipitated by alkaline phosphates from their hydrochloric solution. A separation of the mercury from many other metals, may, however, be pretty readily effected by precipitating the solution of the mixed metals with phosphate of soda, then adding a solution of chloride of sodium in excess, and filtering; the mercury is dissolved under these circumstances, whilst the other metals remain undissolved in form of phosphates.

METHOD FOR THE DETERMINATION OF UREA IN URINE.

The methods just described for the determination of chloride of sodium and of mercury are mainly calculated for the determination of chloride of sodium and urea in urine, and are, perhaps, of particular value for this purpose only.

I will now proceed to describe a new method of determining urea in urine, which equals those now in use, in point of accuracy, but has this advantage, that it far excels them as regards rapidity of execution, and that its application does not require any particular skill, so that it is particularly applicable, as I think, for medical purposes, as a means of assisting the diagnosis of certain states of disease.

This method is based on the fact that urea is precipitated by nitrate of protoxide of mercury.

On gradually adding to a dilute solution of urea an equally dilute solution of nitrate of protoxide of mercury, and neutralizing the free acid of the mixture from time to time by baryta-water or dilute carbonate of soda, a flocculent, snow-white precipitate is obtained, which is insoluble in water. If the addition of the salt of mercury and of carbonate of soda, be continued alternately, as long as this precipitate is formed, a point is arrived at, when by the addition of the carbonate of soda, the mixture, or the spot with which the drop comes in contact, assumes a yellow colour of hydrated oxide of mer-

cury, or basic nitrate of protoxide of mercury. When filtered at this point, the liquor no longer contains any appreciable quantity of urea; all the urea is precipitated. I have subjected to analysis this precipitate, which differs by its amorphous condition from the above-described compounds of urea and nitrate of protoxide of mercury, and I found it in every instance to contain 4 equivs. of protoxide of mercury for 1 equiv. of urea. By mixing a solution of urea with a solution of mercury, both of known strength, it can easily be demonstrated, that a precipitation of yellow oxide by the addition of carbonate of soda to the mixture, is not produced until a volume of the nitric solution of mercury is added, which contains 77 parts of protoxide of mercury, for 10 parts of urea in the solution of urea; this, however, amounts to 4 equivs. of protoxide of mercury to 1 equiv. of urea.

On adding nitrate of protoxide of mercury to a solution of urea as long as a precipitate is formed, the mixture remains *white* on addition of carbonate of soda; if, however, the original mixture be left quietly for some hours, the appearance of the precipitate is changed; it becomes crystalline; the six-sided tablets of the compound with 3 equivs. of protoxide of mercury are easily recognised in it, and the clear liquid, standing above the crystals, which was previously precipitated white, produces now a *yellow* precipitate with alkalies. The compound with 4 atoms of protoxide of mercury, is reduced in the acid liquor into a compound containing less oxide—that is to say, part of the oxide is redissolved.

In order to ascertain whether the exact quantity of the salt of mercury has been added, necessary for the formation of the urea-compound with 4 atoms of protoxide of mercury, it is requisite to neutralize the liquor with carbonate of soda, after the mercurial solution has been added. If the mixture—for instance, a drop of it on a watch-glass, mixed with a drop of solution of carbonate of soda—remain white, it may be assumed with certainty that free urea is still present in the liquor; only when on mixing the two drops, a yellow skin appears on the surface, the limit is attained, or rather a little exceeded; but a very slight excess of the mercurial solution is required to indicate that the requisite quantity for the precipitation of the urea has been added. From this it is evident that if the amount of mercury in the solution be known, the quantity of urea in a liquid containing it may be estimated by the amount of solution used, in the described manner, for the precipitation of the urea. Or if for the precipitation of a *known* quantity of urea—say 100 milligrammes—a certain volume of solution of mercury be necessary, an equal volume of it will indicate the same amount of

urea in a liquor, the amount of urea in which is unknown. From the volume of this solution, used for the precipitation, the quantity of urea present may be calculated; the consumption of half the volume indicates half as much; that of double the quantity, twice as much urea in the liquor.

On this point also my experiments have yielded perfectly concordant results, as the following numbers will show.

The first series indicates the amount of urea obtained from 10 cub. cent. of the solution by simple evaporation. The second series exhibits the amount of urea in the same volume of the same solution, as found by the determination with the graduated solution of nitrate of protoxide of mercury.

For 10 cub. cent. of solution of urea were obtained:

	I.	II.	III.	IV.	V.	
I. Urea by evaporation	371·5	412·	117·	98	512	milligrms.
II. „ by nitrate of mercury . . .	372·5	412·	116·8	98	512·75	„

The methods for the determination of urea, up to the present time acknowledged as the best, are those of Ragski and Bunsen; both are based upon the same principle—viz., upon the transformation of the urea into carbonate of ammonia. Ragski determines the ammonia in the form of ammonio-chloride of platinum; Bunsen determines the carbonic acid in form of carbonate of baryta. Both methods give very trustworthy results, if in Ragski's method the potassio-chloride of platinum, precipitated simultaneously, be taken into account.

The following series of experiments, in which the amount of urea in urine of man was determined according to Ragski's method, and by means of nitrate of protoxide of mercury, may prove that the latter method is not inferior to the former.

20 cub. cent. of urine of different individuals contained of urea:

Determined by means of	I.	II.	III.	IV.*	
nitrate of mercury	450	360	450	508	milligrms.
Determined by Ragski's method	446	350	457	508	„

I have found on precipitating urine with a mixture of nitrate of baryta and baryta-water, filtering off the phosphate and sulphate of baryta, evaporating the liquid, extracting the residue with alcohol, evaporating the alcoholic extract to dryness, and again exhausting it with absolute alcohol, that this alcoholic solution contains tolerably

* These determinations have been made by my assistant, Dr. Mayer.

pure urea, crystallizing from it in colourless needles. This method may be used to prepare urea directly from the urine without precipitating with nitric acid; and this mode of proceeding may even be used for the quantitative determination, as the following experiments will show, for which the same urine was used as in the above determinations of urea.

	In 20 c. c. of urine.				In 10 c. c. of urine.*			
	I.	II.	III.	IV.	V.	VI.	VII.	
Urea by alcohol	428	326	439	503	223	219	198·5	milligrms.
„ by nitrate of protoxide of mercury	450	360	450	508	225	220	200	„

The solubility of chloride of sodium in alcohol is, however, somewhat increased by urea. According to an experiment made on this point, alcohol dissolved from a mixture of chloride of sodium and urea 1·0085 grms. consisting of 0·9785 urea, and 0·030 chloride of sodium. 100 parts of the dissolved substance contained accordingly 2·97 of chloride of sodium, and 9·703 of urea.

Finally I determined the urea by means of nitrate of protoxide of mercury in the urine of different persons, and then, in order to test the influence of the other constituents of urine, I mixed the same urine with weighed quantities of pure urea, and determined the latter again: the following results will show that these other constituents exert no influence in the determination.

10 cub. cent. of urine contained:

	I.		II.		III.		
Urea	272	372	212	462	170	195	milligrms. of urea.
After adding	100		250		25		
The second determination gave		373		464		196	„ „ „

In all the experiments with the test-liquor, the urine was previously precipitated with a mixture of baryta-water and nitrate of baryta, an operation which was omitted in the application of Ragski's method.

Preparation of the solution of Mercury, which serves for the precipitation of Urea in Urine. — 4 grms. of pure urea are first dissolved in water, and diluted with water until the volume of the solution amounts to exactly 200 cub. cent. (by dissolving 4 grms. of urea in 200 cub. cent. of water, 201·75 cub. cent. of liquor would be obtained, an excess of 1·75 cub. cent.)

20 cub. cent. of the solution of nitrate of protoxide of mercury, to be used for the determination of urea in urine, should exactly suffice to indicate with precision the urea in 10 cub. cent. of the solution of

* These determinations were made by my assistant, Dr. Mayer.

urea just described, containing 200 milligrammes of urea: 1 cub. cent. of it should correspond to 10 milligrammes of urea. For this purpose the solution of mercury should contain a quantity of oxide sufficient to form with 100 milligrammes of urea, the nitrate with 4 equivs. of protoxide of mercury, besides a small excess of protoxide of mercury, for the purpose of indicating the complete precipitation of the urea; so that, on adding the last drop of the 10 cub. cent. of solution of mercury to the solution of urea, a distinct yellow colour is perceptible, when a few drops of the mixture are mixed with solution of carbonate of soda.

I have found by a series of experiments that for 100 milligrammes of urea, which require, according to calculation, 720 milligrammes of protoxide of mercury (in the form of nitrate), 10 cub. cent. of the solution of mercury should contain 772 milligrammes of protoxide of mercury, in order to produce a distinct reaction of protoxide of mercury in dilute liquids. Every cub. cent. of the liquor should, therefore, contain an excess of 5·2 milligrammes of protoxide of mercury. The test-liquor is best obtained by dissolving pure metallic mercury in pure nitric acid in a beaker; keeping the mixture heated, with frequent addition of some nitric acid, until no longer any trace of nitrous vapours escape; then evaporating to the consistence of a syrup in the same vessel, or a water-bath, and lastly diluting with water, until 100 cub. cent. of the dilute liquor contain exactly 7·140 grms. of mercury. This is the case when for 100 grms. of mercury (converted into nitrate of the protoxide), as much water is added as will bring the volume of the liquor to 1400 cub. cent.

When for the preparation of the nitrate of the protoxide, crystallized nitrate of suboxide of mercury is used, which may with greater facility be obtained in a state of purity and free from other metals than metallic mercury, and a concentrated solution of the salt of the protoxide of unknown strength is thus produced, the amount contained in it has to be determined, and the solution reduced by water to the proper degree. This is done by means of the method described, p. 14. Or a known volume of the concentrated solution is diluted with 10 times its bulk of water, and the amount of protoxide of mercury determined in 10 cub. cent. of it, by precipitation with potassa, or in the form of sulphide of mercury, by mixing the solution with a solution of sulphate of soda, and passing sulphuretted hydrogen through it, till the precipitated basic sulphate of protoxide of mercury is decomposed.

Previous to its application for determining the urea in urine, the dilute solution of mercury must be tested as to its correctness by

means of a solution of pure urea; for this purpose we may use the solution of urea, mentioned above, containing in 10 cub. cent. 200 milligrammes of urea.

It is advisable, in diluting the concentrated solution of mercury not to reduce it, by the addition of water, at once to the calculated degree; but to add rather less water at first, then test it with the solution of urea, and complete the process.

The best mode of proceeding is, to dilute 10 cub. cent. of the concentrated solution of mercury with 5 or 10 times its volume of water, according to concentration, and to determine approximately the amount of protoxide in 10 cub. cent. of this dilute solution, by means of phosphate of soda and the graduated solution of chloride of sodium.

Suppose, for 10 cub. cent. of the five times diluted solution of mercury, 18·5 cub. cent. of solution of chloride of sodium have been used; the amount of water to be added may then easily be calculated.

For 10 cub. cent. of the concentrated solution should be used 38·5 cub. cent. of solution of chloride of sodium (corresponding to 772 milligrammes of protoxide of mercury); there have been actually used $5 \times 18{\cdot}5 = 92{\cdot}5$ cub. cent. of the solution of chloride of sodium. If then 92·5 cub. cent. solution of chloride of sodium be used for 10 cub. cent. of the concentrated solution of mercury, then exactly 4·16 cub. cent. of it are necessary for 38·5 of solution of chloride of sodium. If, therefore, 416 vols. of the concentrated solution of mercury be mixed with 584 vols. of water, 1000 vols. of a dilute solution are obtained, 10 cub. cent. of which correspond exactly to 38·5 cub. cent. of solution of chloride of sodium.

It is, as before stated, advisable, not to add the calculated quantity at once, but rather less. 10 cub. cent. of the normal solution of urea are now measured off, and then from a burette the approximatively diluted solution is added, until a few drops on a watch-glass produce a distinct yellow colour with carbonate of soda. Suppose 19·25 cub. cent. of the solution of mercury were used for this purpose; then for 192·5 cub. cent. of the solution, 7·5 cub. cent. of water have to be added, and with this solution another trial experiment is made. When, after the addition of 20 cub. cent. the appearance of the yellow colour is distinct, the solution of mercury may then be used for determining the urea in urine.

Every possible care must be bestowed on the correctness of the test-liquor, inasmuch as it replaces a balance with which, when defective, the weighings made are the more incorrect, the smaller

the differences in the weights which have to be determined. In the case of an incorrect balance, the error may be met at each weighing; accurate weighings may be made with it; but in the case of a graduated liquid, the corrections must be made before it is used. The volume of the liquor does not add to the trouble, and it is therefore advisable to prepare as large quantities as possible at one time.

The slight excess of the protoxide of mercury in the test-liquor is like the index of the balance; the yellow colour is its deflection, the amount of which must be carefully noted.

The test-liquor is graduated with a solution of urea containing 2 per cent of this substance; 15 cub. cent. of this solution of urea require for the precipitation of the urea, and for indicating its termination, 30 cub. cent. of solution of mercury; 45 cub. cent. mixture are obtained, containing in the whole $30 \times 5{\cdot}2 = 156$ milligrammes of free protoxide of mercury; every cub. cent. contains therefore 3·47 milligrammes of protoxide of mercury.

If the 15 cub cent. of solution of urea contain 4 per cent of urea, and to 15 cub. cent. of it 60 cub. cent. of solution of mercury be added, a mixture of 75 cub. cent. is obtained, containing 312 milligrammes of protoxide of mercury; in every cub. cent. 4·16 milligrammes; there is, therefore, an excess of 0·69 milligramme of protoxide of mercury required to produce the original colour.

Careful experiments have proved that, in analyses of urine, when the amount of urea is increasing, an error is committed, tending to diminish the amount of urea; in the case just mentioned, only 59·37 cub. cent. instead of 60 cub. cent. of solution of mercury would be added to make the original colouring appear. In order to remove this error, an addition has to be made—for 15 cub. cent. of urine, and before the test is applied—of ½ cub. cent. of water for every cub. cent. of solution of mercury which has been used over and above 30 cub. cent.; if, for instance 20 cub. cent. more than the 30 cub. cent. be required, we have to add 10 cub. cent. of water. It will always be found that, after the addition of the water, a few drops of the solution of mercury have to be added in order to produce the proper indication.

For the same reasons, when the quantity of urea in urine amounts to 1 per cent only, 15·3 cub. cent. and not 15 cub. cent. of the solution of mercury must be added to 15 cub. cent. of urine, in order to obtain the test; to remove this error, which increases the amount of urea, a deduction has to be made, in the more dilute urines, of 0·1 cub. cent. for every 5 cub. cent. of solution of mercury, used less than 30 cub. cent. If, therefore, 25 cub. cent. of solution

of mercury have been used for 15 cub. cent. of urine, the amount, 249 milligrammes, is expressed by 24·9 cub. cent. of solution of mercury, &c.

For the purpose of determining the urea in urine, a mixture of 2 vols. of baryta-water and 1 vol. of solution of nitrate of baryta, both saturated whilst cold, is first prepared, and 1 vol. of this alkaline liquor mixed with 2 vols. of urine. Here a small glass cylinder of optional capacity is conveniently used, which is first twice filled with urine to overflowing. The aperture of the cylinder is each time covered with a glass plate, causing the excess to flow off; the same cylinder is then filled once with the solution of baryta, and this added to the urine in a beaker. On mixing both liquors, a precipitate is formed, which is filtered off. 15 cub. cent. of the filtered liquor are measured off for each analysis, corresponding to 10 cub. cent. of urine.

To this volume of urine, without previously neutralizing, the graduated solution of the nitrate of protoxide of mercury is added from a burette, the liquor being constantly stirred, and the test applied when no further precipitate is observed, viz., no further thickening of the liquor. To this end, a few drops of the liquor with the precipitate are put into a watch-glass, and then a few drops of solution of carbonate of soda added, proceeding from the rim of the watch-glass; this is best done by means of a pipette of Indian-rubber.* If, after some minutes, the mixture retain its white colour, a further quantity of solution of mercury is to be added; and this process is continued till a fresh sample from the glass exhibits plainly the yellow colour after the addition of carbonate of soda.

The number of cub. cent. is then read off, and the figure obtained corrected, as described above, according to the contents of the urine.

Method of determining Urea in Urine containing Chloride of Sodium.—A series of experiments have proved that the amount of chloride of sodium in urine, when it reaches 1 to 1½ per cent, exercises an influence on the determination of urea by means of nitrate of protoxide of mercury. When 20 cub. cent. of the graduated solution of mercury are added to 10 cub. cent. of the solution of pure urea, carbonate of soda produces in this mixture a distinct yellow colour of precipitated protoxide of mercury; if now 100 to 200 milligrammes of chloride of sodium be added to the mixture, and the test again applied, the yellow colour does not make its appearance

* See Mohr's Lehrbuch d. Pharm. Tech. 2 ed. 1853, p. 397.

on the addition of carbonate of soda; and in order to reproduce it, $1\frac{1}{2}$ to $2\frac{1}{2}$ cub. cent. of the solution of mercury have to be added. The determination shows, therefore, 15 to 25 milligrammes of urea too much.

Just the same occurs with urine. Of the many experiments which I have made on this point, I select the following, in order to show plainly this influence: In one portion of urine the amount of chloride of sodium was first determined; then, in an equal quantity, the urea by means of nitrate of protoxide of mercury. This determination was repeated with an equal volume of urine, after the chlorine had been removed by nitrate of silver; finally, the urea was determined according to Ragski's method in the same quantity of urine.

10 cub. cent. of urine contained milligrammes of urea:

	Chloride of sodium.	Before removing the chlorine.	After removing the chlorine.	According to Ragski's method.
I. . .	145	245	225	223
II. . .	155	210	180	175
III. . .	135	245	225	225·5

In Experiment I. the test indicated, before the chlorine was removed, 20; in II. 30; in III. 20 milligrammes of urea more than was actually contained in it. When the quantity of chloride of sodium amounts to more than 2 per cent., this error does not proportionally increase, but remains constant within certain limits.

It has been seen from the method of determining chloride of sodium by means of nitrate of protoxide of mercury, that a solution of urea containing chloride of sodium is not precipitated by nitrate of protoxide of mercury, until the chloride of sodium is completely transformed into corrosive sublimate. In a solution of 200 milligrammes of urea, and 10 milligrammes of chloride of sodium in 10 cub. cent. of water, to which have been added 20 cub. cent. of the solution of mercury, the excess of the salt of mercury (which would have produced the yellow colour on addition of carbonate of soda) is not contained in form of nitrate, but of corrosive sublimate, and it is evident that the change in the indication is effected by the formation and presence of the corrosive sublimate. Instead of 3·46 milligrammes of protoxide of mercury in the form of nitrate, the mixture contains the same amount of oxide in the form of corrosive sublimate.

On diluting a solution of corrosive sublimate with water, until it yields with carbonate of soda a distinct brownish-yellow precipitate of

oxychloride of mercury, then mixing the same solution of sublimate with a drop of nitric acid, and adding it to the carbonate of soda, the mixture of both remains clear; no precipitate is formed, or at most only a slight whitish cloudiness, from which, after long standing, single brownish-yellow tablets are deposited. In this condition, however, the excess of corrosive sublimate is contained in the mixture of the solutions of urea and of mercury; it contains the greater portion of the nitric acid of the latter in an uncombined state.

By this nitric acid, part of the carbonate of soda is converted into bicarbonate, which does not precipitate corrosive sublimate. When the mixture contains a larger amount of corrosive sublimate, in consequence of a larger amount of chloride of sodium in urine, the liberated carbonic acid is not sufficient to prevent the precipitation of all the protoxide of mercury; a brownish-yellow precipitate is now formed. This appears to me to be the cause why the indication of the complete precipitation of the urea is deferred, by the presence of a certain quantity of chloride of sodium, and why the limit of the reaction is not still further removed, when the amount of chloride of sodium is increased.

With urine containing 1 to 1½ per cent of chloride of sodium, the correct number of milligrammes of urea in 10 cub. cent. of urine may be obtained at once by subtracting 2 cub. cent. from the number of cub. cent. used for the solution of mercury; and even when the amount of chloride of sodium in the urine of different individuals varies within certain limits, the differences obtained in the amount of urea are still correct, and comparable with each other; only in the absolute quantity there is an error which, uncorrected, amounts to 15 to 20 milligrammes for 10 cub. cent. of urine.

In determinations in which the absolute quantity of urea in urine is of importance, the chlorine in the urine must be removed, and the chloride of sodium converted into the nitrate; this is done by means of nitrate of silver. For this purpose a solution of silver is prepared from 11·601 grms. of fused nitrate of silver, which are dissolved in water and diluted until the volume of the solution amounts to 400 cub. cent. 1 cub. cent. contains 29·01 milligrammes of nitrate of silver corresponding to 10 milligrammes of chloride of sodium.

The solution of mercury, the preparation of which has been already described, pp. 8, 9, corresponds with this solution of silver; both indicate, when used in equal volumes, the same amount of chloride of sodium. If, therefore, 12·5 cub. cent. of the solution of mercury had to be added to 10 cub. cent. of urine until the appearance of

the cloudiness, the chlorine in the same volume of urine will be completely separated by 12·5 cub. cent. of silver-solution, whilst no silver remains dissolved.

Since the quantity of silver-solution to be added to the urine containing chloride of sodium, for the removal of the chlorine, may be ascertained in a few seconds by means of the solution of mercury, this operation loses all inconvenience, whilst otherwise it would be tedious, and require much time.

Suppose, for 15 cub. cent. of the urine precipitated by the solution of baryta (containing 10 cub. cent. of urine), 17·5 of solution of mercury had been used; then with the pipette, 30 cub. cent. of the same urine are measured off, and 35 cub. cent. of the solution of silver are added; the liquor is then at once filtered, and of the filtrate always one half of the sum of the mixed liquors taken for the test; in this instance, therefore, 32·5 cub. cent. contain 10 cub. cent. of urine. These are now mixed with the graduated solution of mercury, and the amount of urea ascertained in the manner described, taking into consideration the dilution in consequence of the solution of silver added.

The numerous experiments made by Professors Dr. Vogel and Dr. Bischoff, at whose instigation this method has been devised, leave no doubt as to its applicability and correctness. In describing such a proceeding, numerous difficulties present themselves, which in practice prove to be insignificant; indeed, the description is much more complicated than the execution.

The remarkable simplicity which this method of determining urea and chlorine has attained, is mainly owing to the deep interest which my two excellent friends have bestowed upon my experiments; it is the result of a whole series of methods, which one after the other were rejected, not so much for want of accuracy, but on account of the greater difficulty of execution; and on this occasion I have very plainly seen how important and requisite it is for the purpose in view, when the chemist is solving a physiological problem, does not work by himself alone, but in conjunction with a pathologist and a physiologist.

Chemists will observe that, by this determination of urea, mercury and chloride of sodium, another very interesting problem has been solved—viz. the determination by weight of chloride of sodium, mercury and urea, without having recourse to a balance. The paradox of a determination by weight without weighing, disappears by the consideration, that a solution of chloride of sodium, saturated at the ordinary temperature, contains a definite, unchanging weight

of chloride of sodium, and that in 10 cub. cent. exactly 3 184 grms. of chloride of sodium are obtained; by dilution with the proper quantity of water, a solution of chloride of sodium is obtained, containing in 1 cub. cent., 10 or 10·852 milligrammes of chloride of sodium. With these solutions, nitrate of protoxide of mercury may be graduated for the determination of chlorine, mercury and urea, without the necessity of using other instruments than a burette and a pipette.

ADDITIONAL REMARKS.

In order to prevent the rapid transformation of urea into carbonate of ammonia, it is requisite, when collecting the urine of animals kept in cages, to wash the bottom of the cage, if made of wood, from time to time, with some dilute nitric acid, and to put a few drops of nitric acid into the vessel in which the urine is collected.

With urine of man and of the dog, 1 vol. of solution of baryta to 2 vols. of urine is generally sufficient to remove all the phosphoric and sulphuric acids, and to leave some baryta in solution. If, however, the urine be alkaline from the presence of an alkaline carbonate, which may be under certain circumstances carbonate of ammonia derived from decomposed urea, 1 vol. of solution of baryta to 2 vols. of urine does not suffice; in such cases, to precipitate all the carbonic acid, more solution of baryta has then to be used.

When 3 vols. of solution of baryta are mixed with 4 vols. of urine, 17·5 cub. cent. of the liquor filtered off (corresponding to 10 cub. cent. of urine) must be taken for the determination of urea. Of a mixture of equal volumes of solution of baryta and of urine, 20 cub. cent. must be taken for the test, and so on.

I have investigated the influence of the putrefaction of urine on this method of determining the urea, and have frequently obtained the same results with putrid urine, provided the decomposition had not progressed too far, as with the same urine in the fresh state. If, after the addition of 19·5 cub. cent. to the fresh urine, the yellowish colour of the protoxide of mercury made its appearance, the same reaction ensued with urine which had stood for one or two days, after using the same portion of solution of mercury. This can, however, not be depended upon, as the following results will show.

For the precipitation of urine with nitrate of protoxide of mercury were used, for:

10	cub. cent.	of urine, whilst fresh . .	27·	cub. cent.	of solution of mercury.	
10	„	„ of the same urine, after having stood for one day .	27·	„	„	„
10	„	„ of the same urine, after the third day	27·5	„	„	„
10	„	„ of the same urine, after the fourth day	28·	„	„	„

For another sample of dog's urine there were used, for:

10	cub. cent.	whilst fresh . .	36·5	cub. cent.	of solution of mercury.		
10	„	„ two days old .	41·	„	„	„	„
10	„	„ three days old .	42·	„	„	„	„
10	„	„ four days old .	42·	„	„	„	„

One equivalent of urea yields by its putrefaction 2 equivs. of ammonia; and if, by adding the solution of mercury, the compound described by C. G. Mitscherlich and Kane were formed, which contains 2 equivs. of mercury for 1 equiv. of ammonia or amidogen, just as much of the solution of mercury would be required for its precipitation as for the urea from which the ammonia has been formed. The experiments show, however, that somewhat more is required, which seems to indicate that, under these circumstances, ammoniacal compounds, with 3 and perhaps more equivs. of protoxide of mercury, are formed.

For exact determinations, no other resource is left than to determine the quantities of urea and of ammonia present, each separately, and to express the ammonia found, as urea. For this purpose, two portions of urine are taken; the first of which is used for the determination of the urea, the other for that of the ammonia.

In estimating the urea in this urine, it is not precipitated with the usual mixture, but only with baryta-water; of the liquor filtered off, a volume is taken, containing 10 cub. cent. of urine, and this is then heated in a water-bath, until no further escape of ammonia is perceptible. Since, after the treatment with baryta, the ammonia is in solution in form of caustic ammonia, its expulsion is readily effected; care is, of course, to be taken, that all the carbonate of ammonia is decomposed, and the addition of the baryta-water has to be regulated accordingly.

In the other portion of the urine, the ammonia is determined by means of one of the ordinary alkali-metrical methods. For this purpose it is best to use a dilute sulphuric acid, made with 16·333 grms. of pure hydrated sulphuric acid and so much water that the

mixture occupies 500 entire, or 1000 half cub. cent. ½ cub. cent. of this sulphuric acid saturates exactly 5·66 milligrammes of ammonia; this is the quantity formed from 10 milligrammes of ammonia; 1 cub. cent. of this sulphuric acid used in saturating the ammonia in urine corresponds therefore to 20 milligrammes of urea.

These determinations are somewhat more precise when a measured volume (containing a known quantity of urine) of the urine, treated with baryta, is submitted to distillation, and the product collected in a receiver, containing a measured volume of the above dilute sulphuric acid, which must be larger than is requisite to neutralize the ammonia passing over; the quantity of free acid left is then determined by means of a dilute solution of ammonia, graduated for the dilute sulphuric acid. Thus, if 40 cub. cent. of the dilute sulphuric acid have been put into the receiver, and afterwards 15 cub. cent. of the graduated solution of ammonia were required to saturate the free acid left, a quantity of ammonia was obtained by the distillation corresponding to 40−15=25 cub. cent. of the dilute sulphuric acid, or to 250 milligrammes of urea.

II.—*On the Mode of Estimating the Value of Red Prussiate of Potash.*

By Francis Lieshing.

If the red prussiate were always sold in the form of large crystals, as it usually occurs, the valuation of it would scarcely be required. Since, however, large quantities of this salt are prepared by saturating the powdered yellow prussiate with chlorine, and the product obtained (which necessarily must contain a certain amount of chloride of potassium, and besides frequently contains a portion of undecomposed yellow prussiate) is sold in a powdered state, it becomes a matter of importance to have an easy method of determining the real amount of pure ferricyanide of potassium it contains, and likewise of checking any adulteration with other ingredients.

The methods of valuation, which, on account of facility and quickness of performance, have lately become very useful, are the so-called alkalimetric methods of estimation; and it is this direction that I have followed to obtain a test for the ferricyanide of potassium.

If the object is merely to compare several samples of red prussiate as to their relative value, or to compare them with a standard of a pure

and carefully dried drug, a diluted solution of sulphide of sodium, containing a considerable excess of the alkali, may be employed. A certain weight, say 50 or 100 grains, of the pure ferricyanide is dissolved in a few ounces of water, and into this a diluted alkaline solution of sulphur is poured in small portions from an alkalimeter. By each addition, a quantity of sulphur is precipitated, forming a milky liquid, which is of the purest white at the very point of saturation—that is to say, when all the ferricyanide has been converted into ferrocyanide. To determine, however, this point more accurately, a strip of white filtering paper, dipped beforehand into a solution of acetate of lead, and dried, is introduced into the liquid. So long as any red prussiate is present, the paper will remain white, but the slightest excess of the sulphide will give it a brownish tinge. After noting the number of measures consumed, the same solution of sulphur is applied to the samples about to be tested; or it may be diluted before this, so that each measure shall correspond to $\frac{1}{2}$ grain or $\frac{1}{4}$ grain of pure prussiate. If any of the samples should contain metallic admixtures, this would at once be indicated by the test. The liquid would in this case appear white at the very point of the complete transformation of the ferricyanide, but the next drop of the sulphuret added would colour it.

The reaction which takes place in the process described is the following: 1 equiv. of ferricyanide of potassium $= K_3 Fe_2 Cy_6$ decomposes 1 equiv. of sulphide of sodium by taking up 1 equiv. of sodium, and thus forming 2 equivs. of ferrocyanide of potasssium $= \left.\begin{matrix}3K\\Na\end{matrix}\right\} Fe_2 Cy_6 + 6HO$, in which 1 equiv. of K is replaced by 1 equiv. of Na.

The soluble iodides are likewise decomposed by red prussiate in the same way as the sulphides, and iodine is set free. This is especially the case when the mixture is heated.

In order to obtain, however, a test of more stability and better fitted for preservation than the sulphide of sodium, I prepared and tried the following three compounds:

Sulphantimoniate of sodium ($3\,NaS\,.\,Sb\,S_5 + 18\,HO$),
Sulphostannate of sodium ($NaS\,.\,SnS_2$), and
Terbasic sulpharseniate of sodium ($3\,NaS\,.\,AsS_5 + 15\,HO$).

But although these three compounds exercise the same decomposing action upon the red prussiate, I found only the sulpharseniate to possess sufficient stability to remain quite unchanged in stoppered bottles for a long period of time.

This compound may be easily prepared, either by dissolving pentasulphide of arsenic in liquid sulphide of sodium, or by dissolving arsenious acid in caustic soda at boiling heat, and adding from time to time a concentrated solution of sulphur in caustic soda, continuing the additions to the boiling liquid, till no further precipitation of sulphur takes place.* After filtering and cooling, a large crop of pale yellow crystals is obtained, which should be separated from the mother-liquor, washed with cold water, dissolved and crystallized again repeatedly, until they dissolve without leaving any residue, and appear perfectly transparent. They are then to be dried upon filtering paper at the common temperature, and preserved for use in a stoppered bottle. The crystals are usually short rhomboidal tables, but they assume a longer columnar form, and become at the same time more transparent, when a little carbonate of soda has been added to the solution. When dried at the common temperature and afterwards heated to 100° C., they lose 33·1 per cent of water of crystallization, and dissolve again, without leaving any residue, or having undergone any decomposition. The solution is pale yellow, and may be kept for a long time without decomposition, especially when mixed with pure carbonate of soda or potash.

The sulpharseniate of sodium is readily decomposed by all acids, as well as by chlorine and by red prussiate of potash. By the action of acids, pentasulphide of arsenic is immediately precipitated, with evolution of sulphuretted hydrogen gas. A neutral solution of red prussiate of potash, when mixed with small portions of a solution of the sulpharseniate, becomes at first only opalescent; by further additions it turns acid, and yellow sulphide of arsenic is then likewise precipitated, with evolution of sulphuretted hydrogen. If, however, either the prussiate or the sulpharseniate has been mixed with a certain quantity of pure carbonate of soda, the pentasulphide of arsenic likewise undergoes decomposition. The liquid becomes milky from separation of pure sulphur, and its green tint turns whiter by each addition, until, after complete transformation of the ferricyanide, it exhibits the purest white. This point of saturation may easily be recognised from the purity of the white; but, to be sure that all the fer*ric*yanide has been converted into fer*ro*cyanide, a few drops of a cochineal-decoction are added, which will immediately be bleached if any fer*ric*yanide is yet present, but in its absence will impart to the liquid a red tinge. In this decomposi-

* It must be remembered here that a much larger quantity of sulphur is required than would appear from the constitution of the salt; since the $As\,O_3$, as well as the $Na\,O$, is to be deoxidized at the expense of the sulphur.

tion no formation of sulphurous or sulphuric acid is observed, the precipitate consists of pure sulphur, whilst the pentasulphide of arsenic is apparently only converted into arsenious acid. The process, when the liquid is not alkaline, is probably as follows: 3 equivs. of ferricyanide of potassium = 3 ($3\,K\,.\,Fe_2\,Cy_6$) will take from 1 equiv. of sulpharseniate of sodium = $3\,Na\,S\,.\,As\,S_5 + 15\,HO$, 3 equivs. of sodium, setting free 3 equivs. of sulphur and 1 equiv. of pentasulphide of arsenic, and forming $\left.\begin{matrix}9\,K\\3\,Na\end{matrix}\right\} Fe_6\,Cy_{18} + 18\,HO =$ 6 equivs. of ferr*o*cyanide of potassium, in which 3 equivs. of K are replaced by 3 equivs. of Na. If, however, the liquid be made alkaline, the carbonate of soda added furnishes 3 more equivs. of sodium, again to form with 3 equivs. of ferricyanide of potassium $\left.\begin{matrix}9\,K\\3\,Na\end{matrix}\right\} Fe_6\,Cy_{18} + 18\,HO = 6$ equivs. of yellow prussiate, the 3 equivs. of oxygen separated from the soda, joining with 1 equiv. of arsenic and forming 1 equiv. of arsenious acid, which again will combine with 1 equiv. of soda.

Assuming thus, that 6 equivs. of red prussiate would form, by the action of 1 equiv. of sulpharseniate of sodium and 3 equivs. of soda, 12 equivs. of yellow prussiate of potash, calculation shows, that for every 100 grains of pure red prussiate, 20 grains of crystallized $3\,Na\,S\,.\,As\,S_5 + 15\,HO$ are required; and this is the exact proportion which has also been found by experiment.

We weigh, therefore, on the one hand 100 grains of the red prussiate to be tested, and dissolve it in 2 ounces of water; on the other, 20 grains of the sulpharseniate and from 40 to 60 grains of pure carbonate of soda or potash; these are dissolved together in the alkalimeter in 400 measures of water, so that each measure consumed (containing $\frac{1}{20}$th of a grain of sulpharseniate) would indicate $\frac{1}{4}$ per cent of pure red prussiate. When after gradual addition the mixture has acquired a pure white, the complete transformation may be ascertained by a drop of cochineal liquor.

Attention must be paid to the circumstance, that all commercial soda contains small quantities of sulphur, which would interfere with the exactness of the test. This is less the case with pearl-ash; but it will be best to employ carbonate of soda or potash especially purified for the purpose.

Whilst in the above process the pentasulphide of arsenic contained in the sulpharseniate of sodium is converted by red prussiate into arsenious acid, it is, on the contrary, converted into arsenic acid by the action of hypochlorite of lime. This will appear from the follow-

ing experiment: If to a solution of arsenious acid in an excess of soda, which has been coloured by a few drops of cochineal-decoction, the slightest quantity of red prussiate be added, the colour will be destroyed immediately, the arsenious acid not serving here as a protection; the same liquid will however keep its tint after considerable additions of hypochlorite of lime. The same behaviour towards hypochlorite of lime is exhibited by a solution of red prussiate after complete transformation by sulpharseniate, whilst an alkaline cochineal-decoction, alone or mixed with yellow prussiate, is immediately bleached by the hypochlorite. It is besides a peculiarity of an alkaline solution of cochineal, that its decolorization by red prussiate or chlorine is instantaneous, and much easier to discern than that of an acid solution. Amongst a number of colouring matters, I found only indigo-carmin in connection with carbonate of soda equally sensible for the above two agents; and this may easily be accounted for, if we remember that indigo-carmin, as well as cochineal, is acted upon and gradually discoloured by alkalies alone.

As to objections which may be made against the sulpharseniate-test, I remark first, that the alkalimetric methods of valuation in general are not sufficient of themselves, and should always be preceded by a qualitative examination of the drug; otherwise the most injurious admixtures might frequently be overlooked. As an illustration of this, I need only refer to the otherwise very accurate test lately proposed by Dr. Penny* for the valuation of tin in the "crystals of tin" and the "double muriate of tin" of commerce, which is based upon the conversion of the protochloride of tin into bichloride by bichromate of potash. In this instance, the liquid "double muriate of tin" might contain a very considerable admixture of protochloride of iron, without even changing its external appearance; and this in practice highly obnoxious admixture, would, by the sole application of the bichromate of potash test, not only escape detection, but the iron would actually be calculated as tin. Supposing then, that certain impurities might occur in the red prussiate, which in acting alike upon the sulpharseniate might give rise to errors, the agents which would require attention, are principally acids, chlorine and hypochlorites, chlorates, sulphides and sulphites, and metallic combinations.

As to the acids, it is evident that their action will be neutralized by the excess of alkali in the test-liquor, and any acidity in the

* Chem. Soc. Qu. J. IV, 239.

prussiate might besides be saturated beforehand by an addition of alkali. The presence of free chlorine and of hypochlorites would be indicated by the smell, and could only occur in a fresh preparation of the powdered kind of red prussiate, the chlorine being neutralized in a short time by the action of the prussiate itself. Chlorates do not seem to have any effect upon the test. Sulphides and sulphites could could not coexist with red prussiate. Metallic compounds would, with few exceptions, either be indicated in dissolving the prussiate, or by the test itself; and as the red prussiate is always first decomposed by the sulpharseniate, the metallic bases would only combine with the sulphide after the point of saturation, and therefore not come into calculation.

Another objection which might be started is, that the carbonated alkali alone might decompose the red prussiate, and that consequently, the quantity to be added is not indifferent. Such a decomposition does in reality take place; but when the mixed solutions are not heated, the action is so slow, that it is scarcely to be observed after a day or two.

It must, however, be allowed that the preparation of the sulpharseniate of sodium, and especially the drying of the crystals, requires much attention; and it would perhaps be preferable to dry them at once at 100° C., and to employ the anhydrous powder.

III.—*On an Improved Assay Balance.*

By George H. Makins.

Having occasion, some little time since, for an assay balance, and being well aware of the points wherein those in use here are deficient, I applied myself to the task of so arranging existing materials, as to produce, if I could, a more effective instrument.

Two forms of assay balances are most common in England. The first is very little more than an exceedingly delicate pair of ordinary scales; in fact, a very light scale-maker's beam, adjusted, as they are accustomed to do, by carefully "setting" it, so as to obtain correct length of arm, and straight line of fulcrum and points of suspension. The second is an instrument imported from France, or better, made here upon the French plan. Of these, the French are but an improvement upon the first class; the beams (of almost all) being permanently adjusted when finished. Those, however, made by

Mr. Oertling upon this plan are furnished with the requisite adjustments, and are very superior in point of detail and workmanship. But the beams of all contain too much metal, and that especially in parts where its presence interferes with their action, by imparting a certain amount of inertia. And, lastly, their stands and movements are very far from convenient.

The essentials in an assay balance appear to be these: first, that it should be constant, so that certain differences of value in weights should always produce the same difference of indication; secondly, it should be exceedingly quick in indicating; and, thirdly, very sensible, and consequently well affected by slight differences.

These two last requirements are somewhat incompatible, for, in proportion as you increase quickness of action, you must diminish sensibility, by lowering the centre of gravity of the system; and it is in the union of these two necessary qualifications that the value of the balance now before the Society lies.

The beam of this balance is what is called a skeleton-beam, 10 inches long, $\frac{1}{2}$ an inch deep at the fulcrum, tapering off to $\frac{1}{3}$ at each end. It is about $\frac{1}{10}$ of an inch thick in the centre, decreasing in the same way to $\frac{1}{20}$ of an inch. As little metal as possible is left in it; thus, in the centre, there is but just enough to allow of secure fixing for the knife-edge; and at the ends, for the adjustments for length of arm, &c. The latter are effected very much in the same way as in Robinson's balance, in which an oblique saw-cut is made nearly through the metal at the ends of the beam, which cut is capable of being opened or closed by pressing-screws. In the present case, a loose piece is put on, and made similarly adjustable by screws. Thus we obtain the adjustment for length of arm.

The bearings for the pendants are two hard steel points, at each end adjustable for the straight line, by having a fine screw cut on each, and provided with fixing-nuts. By these the points can be screwed vertically, up or down, through the horizontal plate formed at the end of the beam.

The pendants are hung on these points by a small steel plate, in the underside of which a cup-shaped cavity is turned for the one, and a groove hollowed out, from the back towards the front, for the other.

Had two cups been employed, it would have been next to impossible, even by the most careful workmanship, to have secured their concentricity with the points. A small steel hook for the pan-chains passes vertically down in a notch in the horizontal plate at the end of the beam.

This last arrangement is due to Mr. Oertling, whom I employed to make this instrument; for in the drawings I sent to him, I had put but a single point at each end, being fully persuaded how much quickness and delicacy are ensured by the least possible friction of the pendants. I had provided against their swinging round, which was almost sure to take place upon a single point, by having the edges of the notches through which they were to pass worked to a kind of knife-edge on each side. Mr. Oertling, however, thought that two would be necessary, and that the friction in them would be less than even if one were used. The weight of the beam, with all its fixed appendages, is only 103 grains. Its bearings are of agate, worked to elliptical surfaces, instead of being as usual, plain. Here, again, but a point of the knife-edge is allowed to bear upon the agate.

Bearing in mind the very small weight these balances would have to carry (and I never load mine with more than 25 grains) I had no hesitation in thus reducing all parts of contact where friction during action occurs, to the smallest possible dimensions, virtually, indeed, to points.

Nor have these parts been found to fail from blunting by wear, as might have been anticipated; at least, in the case of one which I have daily in use, I know that I have made more than ten thousand weighings in it, and not the least diminution of sensibility is as yet observable.

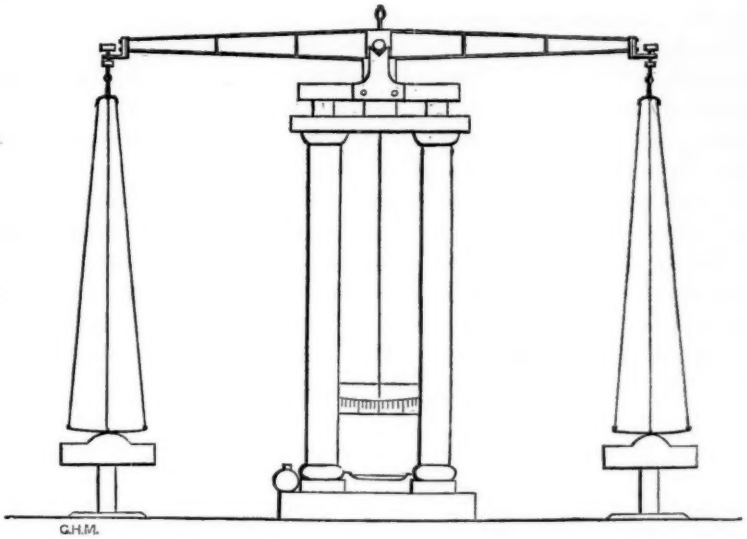
The stand is massive in its construction, in order that when rapidly put into action, no tremulousness may be communicated to the beam.

I give here an outline drawing of the instrument (made to a scale) in order to exhibit its solidity in contrast with the delicacy of the beam and its appurtenances. It consists of two stout pillars, of $\frac{1}{2}$ an inch diameter and $6\frac{3}{4}$ inches long, fixed on a base $\frac{1}{4}$ of an inch thick. Upon the upper end of these is fixed a table, which has two upright pieces rising from it, to which are cemented the agate bearings.

A second corresponding table is attached to the movement rods which pass down the pillars. This table has two mortices in it for the passage of the upright pieces which carry the agates, and upon these uprights it slides up and down. On the outside of this second table is a crutch on each side; these lift off the beam from its bearings when throwing it out of action.

The movement lever on being depressed, first, however, acts upon the arms of two rollers, which are fixed under the lantern, and whose opposite arms depress the ivory tables which support the pans;

this roller motion is particularly free and pleasant in use. By the time the tables are well away, the lever has reached a connecting



stirrup between the movement rods, and begins to drop the beam upon the agates.*

In order to have the smallest possible contact between the under side of the pans and the tables, the latter have hemispherical eminences turned upon them, and the pans themselves have a curve given to them of a radius just equal to the distance between the ivory table and the point of suspension; whereby, should they swing out of the perpendicular during weighing, they will nevertheless be caught by the tables when they rise up to them.

There are adjustments both for the amount of fall of the fulcrum to the agates, and of rise of the ivory tables to the pans; the former is, however, very small in amount.

By the pillars being fixed at a distance of $1\frac{1}{2}$ inch from each other, a good space is obtained for a scale; while, by prolonging the index-needle to rather more than 6 inches downwards, very open degrees are obtained. And besides this great advantage, the motions of the index-needle are brought nearly upon a level with the pans.

To those who are used to a descending index (as in all good

* The movement and "rider" apparatus are both omitted in the above drawing, for the sake of greater distinctness.

chemical balances), the comfort of this arrangement will be at once apparent; for the eye has not to travel a distance between the pans and index (as is the case in the balances to which I just now alluded), but the whole are under view at once.

Much praise is due to the maker for the very beautiful workmanship he has put into these instruments, and that more especially in the beams. Without this perfect degree of execution of the work, they would be uncertain in action, and possess less capability than a heavier instrument.

I have been encouraged by several members who have had opportunities of witnessing its performance, to put a brief description of this instrument before the Society in the form of a notice, and hope that by so doing I have not been occupying time unprofitably. I should have done so last season, but had not one sufficiently long in use to fairly put its powers to the test, before the close of the Society's meetings.

IV.—*On some New Compounds of Tellurethyl.*

(FROM A LETTER OF PROFESSOR WÖHLER TO DR. HOFMANN.)

You are already acquainted with the fact, that some experiments performed at my instigation by Dr. Mallet on telluride of ethyl,* have proved this body to comport itself like an organic radical, like a metal, in fact, and to form both a basic oxide $C_4 H_5 Te O$, and a corresponding chloride, $C_4 H_5 Te Cl$. From the results you obtained by studying the action of iodide of ethyl upon ammonia, the idea suggested itself that this new radical, like ethyl, methyl, &c., might form a tellurethylamine corresponding to ethylamine.

This idea has not, up to the present time, been confirmed by the experiments I have made on this subject; these experiments have led however to the discovery of various compounds, which may be considered as additional proofs of the radical character of telluride of ethyl, and of which I now propose giving you a short account. I may at the same time remark that there appears now a prospect of a more detailed investigation of these remarkable relations, inasmuch as Mr. A. Löwe, of Vienna, whom I also have to thank for

* Ann. Ch. Pharm. LXXIX, 223.

the material employed in these researches, has invented an advantageous process, by which tellurium, till now so rare, is obtained as a by-product in the working of the Transylvanian gold ores, and can thus be introduced in commerce in larger quantity.

1. *Oxychloride of Tellurethyl*, $C_4 H_5 Te O + C_4 H_5 Te Cl$.—This body is produced when chloride of tellurethyl is dissolved in caustic ammonia, or potash, and the solution evaporated to crystallization. It is best to use ammonia, as an excess does not decompose the product. The salt crystallizes easily, as the excess of ammonia evaporates. Chloride of ammonium or of potassium remains in the mother-liquor.

Oxychloride of tellurethyl forms very lustrous, colourless, six-sided prisms, which on heating are decomposed, tellurethyl being separated and metallic tellurium remaining behind. From hot alcohol particularly it may be obtained in beautiful crystals. Hydrochloric acid precipitates from solutions of this substance, colourless oily chloride of tellurethyl, a small quantity of which, with the excess of acid, remain in solution. Sulphuric acid also precipitates chloride of tellurethyl, while sulphate of oxide of tellurethyl remains in solution, from which hydrochloric acid separates another portion of chloride of tellurethyl. Sulphurous acid precipitates from solutions of this oil, a heavy, dark yellow, transparent oil, a mixture of chloride of tellurethyl and of tellurethyl.

From this behaviour, and from the mode of its formation, the composition of this body might have been anticipated; it was however confirmed by analysis. This gave the following numbers:

	Experiment.	Theory. $C_8 H_{10} Te_2 Cl O$.
Carbon . . .	19·94	20·89
Hydrogen . . .	4·96	4·35
Tellurium . . .	56·22	55·87
Chlorine . . .	15·49	15·43
Oxygen . . .	3·39	3·43

This body is therefore formed by the alkali replacing in two equivalents of chloride of tellurethyl, half the chlorine by oxygen.

2. *Bromide of Tellurethyl*, $C_4 H_5 Te Br$, is formed when a solution of the above chlorine-compound, or of nitrate of tellurethyl, is mixed with hydrobromic acid. It separates as a pale yellow, very heavy colourless oil.

3. *Oxybromide of Tellurethyl*, $C_4 H_5 Te O + C_4 H_5 Te Br$, is ob-

tained by dissolving the bromide in ammonia. It crystallizes in shining, colourless prisms, of the same form as the corresponding chlorine-compound, with which it is perfectly analogous.

4. *Iodide of Tellurethyl,* $C_4 H_5 Te I$, may be formed by mixing a solution of nitrate, or of oxychloride or oxybromide of tellurethyl with hydriodic acid. It is also formed when free chloride of tellurethyl is supersaturated with this acid, a reaction which explains why, in the decomposition of the oxychloride, iodide of tellurethyl alone is produced, instead of a compound of this body with the chloride. The salt separates in the form of a very fine yellow precipitate, which on washing and drying becomes an orange-yellow powder. When heated in water, it melts at 50° C. to a heavy yellowish-red liquid, which on cooling solidifies to a yellowish-red, opaque, scaly, frangible mass, soluble in hot alcohol, from which it crystallizes in long, thin, orange-yellow prisms. It is only sparingly soluble in water. When heated above its fusing-point, it decomposes, yielding a yellowish-red oil, a black sublimate, and metallic tellurium. If in its preparation a partially decomposed solution of hydriodic acid is employed, an almost blood-red precipitate is obtained, containing most probably a higher iodide.

5. *Oxyiodide of Tellurethyl,* $C_4 H_5 Te O + C_4 H_5 Te I$.—This body is prepared by dissolving the iodide in ammonia and allowing it to evaporate spontaneously. It crystallizes readily as the excess of ammonia volatilizes, being readily soluble in this, but only sparingly so in water; it forms pale yellow transparent prisms, isomorphous with the corresponding chlorine and bromine-compounds; the surface becomes orange-yellow on exposure to air. Hydrochloric acid separates from an aqueous solution of this body a yellowish-red heavy mixture of chloride and iodide of tellurethyl. Sulphuric acid precipitates orange-yellow iodide of tellurethyl; from the filtrate, hydrochloric acid afterwards separates colourless chloride of tellurethyl. Sulphurous acid precipitates from the solution of the compound an easily fusible, semi-solid mixture of iodide of tellurethyl and tellurethyl.

It was considered superfluous to analyse these compounds, as their composition is clearly established by their behaviour, and from their mode of formation.

No compound could be obtained with cyanogen.

6. Hydrofluoric acid added to solutions of the oxychloride, throws down chloride of tellurethyl, a soluble fluorine-compound remaining in solution, which may be crystallized by evaporation; the same compound is obtained from free oxide of tellurethyl and hydrofluoric

acid; a deportment in which fluorine again deviates much from the other salt-radicals.

7. *Sulphate of Oxide of Tellurethyl*, $C_4H_3TeO.HO + C_4H_5TeO.SO_3$. —This compound was obtained by adding a neutral hot saturated solution of sulphate of silver to a solution of recrystallized oxychloride of tellurethyl, as long as chloride of silver was formed. The new salt crystallizes in groups of small, short, colourless prisms, easily soluble in water. Sulphurous acid precipitates from its solution a yellow oily body, of a most disagreeable odour. Chloride of barium precipitates sulphate of baryta and reproduces the oxychloride. The percentage of sulphuric acid found was 15·10, the above formula requiring 15·91 per cent.

8. *Oxalate of Oxide of Tellurethyl*, $C_4H_5TeO.HO + C_4H_5TeO.C_2O_3$, was obtained by digesting a hot saturated solution of the oxychloride with excess of oxalate of silver. The salt crystallizes in small groups of short colourless prisms, difficultly soluble in water. On heating it fuses, boils, gives off much tellurethyl and a crystalline sublimate, and leaves metallic tellurium. The percentage of oxalic acid found was 14·86, that of tellurium 51·31; the above formula requires respectively 14·56 and 51·87 per cent.

These two salts, which exhibit an acid reaction, may therefore be considered as double salts, consisting of the neutral sulphate or oxalate combined with hydrated oxide of tellurethyl. I leave it for the present undecided whether the base contained in them is identical with the one obtained by Mallet by direct oxidation of tellurethyl with nitric acid, or by decomposition of the chloride with oxide of silver, or whether its atomic weight is doubled, and the sulphate should be expressed thus: $C_8H_{10}Te_2O_2 + HO.SO_3$.

9. *Oxide of Tellurethyl.*—It appears impossible to solate the base without partial decomposition. It was tried in two ways—namely, first by decomposing the oxychloride with freshly precipitated oxide of silver, and secondly, by precipitating the sulphate with hydrate of baryta. In both cases, an alkaline solution of hydrated oxide of tellurethyl, free from baryta and oxide of silver was obtained, which, however, on evaporation on a water-bath, always evolved an odour of tellurethyl, and left at last a thick viscid mass, of the consistence of turpentine, which would not become solid, and which at this stage of concentration suddenly decomposed with effervescence, as if carbonate had been formed, and was decomposed under these circumstances. When treated with acid, the mass evolved carbonic acid at first, but not after some time; it did not altogether dissolve again in water. With chloride of ammonium it evolved ammonia. Hydrochloric acid

precipitated from its solution oily chloride of tellurethyl. The oxide appears to be insoluble in a concentrated solution of potash; for if some of the crystalline oxychloride is heated with the latter, colourless oily drops separate, which possess the odour of tellurethyl, and redissolve on addition of water.

In the next number of the "Annalen" you will find my researches on this subject in detail. As it is to be foreseen that these relations will recur with methyl and the other alcohol-radicals, I have, in consideration of the fecundity of this subject, given a full account of the method of preparing telluride of potassium, tellurethyl and chloride of tellurethyl, as a guide to those who may wish to pursue this investigation.

V.—*Description of an Apparatus for Collecting Gases over Water or Mercury.*

By W. M. Williams.

This apparatus is intended to supersede the cumbrous and expensive pneumatic trough and its appendages. It is constructed on the principle of a common wash-bottle, a flask or tube for generating the gas being fitted to the tube corresponding to that to which, in the wash-bottle, the mouth is applied. It may be constructed either with a three-necked bottle, as in Fig. 1, or a common wide-mouthed bottle of sufficient size, as in Fig. 2. In both figures, *A* represents the bottle used as a receiver; *B* the tube to which the generating flask is attached, which terminates in the upper part of the receiver, and may be called the *gas-tube*; *C* is the tube through which the water is forced; this tube, which dips to the bottom of the vessel, we may call the *water-* or *mercury-tube*. Besides these, there is in the apparatus represented in Fig. 2, a short straight tube *D*, fitted into the cork of the receiver,

FIG. 1.

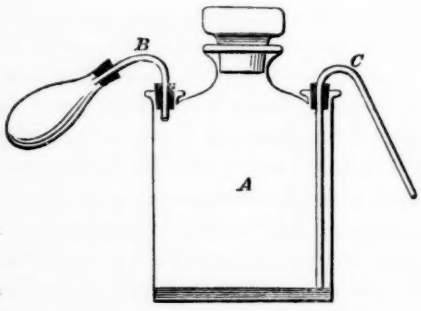
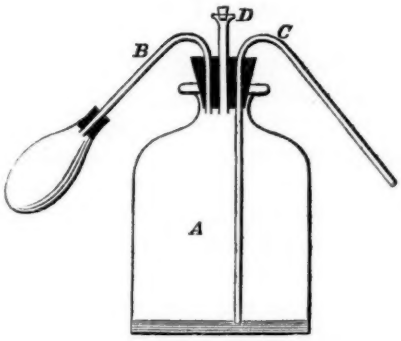


FIG. 2.



its lower part terminating like the gas-tube, in the upper part of the receiver. This tube, which is corked or stoppered, may be called the *filling-tube.*

The mode of using the apparatus is very simple and obvious. Suppose we wish to prepare oxygen gas and demonstrate its properties. The receiver is filled with water, and the flask or tube containing the mixture of chlorate of potash and oxide of manganese, fitted by a cork, to the gas-tube, and heat applied; as the gas is generated, it passes through the gas-tube into the receiver, displacing the water by forcing it up the water-tube. The use of the filling-tube *D* is to get rid of the atmospheric air which comes off at first; this is done by taking out the stopper and refilling the receiver with water after the first portion of the gas has been evolved. In the three-necked apparatus, Fig. 1, the middle stopper is used for this purpose. This may be used for demonstration without removing the gas- and water-tubes (on which account the water-tube should be kept as close to the side of the receiver as possible) by simply taking out the middle stopper, which should be large enough to admit the spoon, &c., required in the experiments.

In the apparatus Fig. 2, the cork and all the tubes must be moved together; and when the gas is to be used immediately, it will be found convenient to slip a piece of plate-glass over the neck of the receiver, with the left hand, at the moment the cork holding the tubes is removed with the right. When the gas is to be kept for any length of time, of course a stopper will be requred.

A number of bottles may be thus filled with gas by connecting them as a series of receivers, the water-tube of the first being attached by a caoutchouc tube to the gas-tube of the second, and so on. The first only need be filled with water or mercury, which successively fills all the rest as the gas displaces it.

In constructing the apparatus, care should be taken not to make the gas-tube too long, in order that it may easily bear the weight of the generating flask; also to bend it at such an angle as to place the flask at a convenient height for the spirit-lamp, the retort-stand, as well as the retort and pneumatic trough, being thus dispensed with.

The water- or mercury-tube should not be carried too high before bending, in order to avoid unnecessary pressure from the column of fluid to be raised.

The outer end of the water- or mercury-tube should dip into the fluid contained in the vessel which receives the water or mercury driven out, in order to prevent regurgitation of air, which would otherwise take place when the gas in the flask and receiver is cooling, after the generation of gas has ceased.

One of the advantages of this apparatus is the facility with which varying quantities of gas may be collected in the same receiver, as the generation of the gas may be stopped at any stage, when the receiver is a fourth, a third, or half full, and this small quantity of gas experimented upon without disturbing the apparatus; the receiver may then be filled again, more gas made, and so on, any number of times. By taking advantage of this, a mixture of gases in any proportions may be easily made. I have fitted up on this principle a small bottle for exploding the mixture of oxygen and hydrogen gases.

For demonstrating the properties of oxygen on a large scale, a globe might be fitted up on this principle, a layer of sand being kept at the bottom to prevent cracking by ignited iron, &c. The difficulty of keeping sand at the bottom of a globe, which is to be inverted when filled, is by this arrangement obviated.

For collecting gases over mercury, an apparatus fitted up on this principle enables us to attain the minimum of expenditure of mercury; since the quantity required is only equal to the volume of the vessel receiving the gas, and with this any number of such vessels may be filled by connecting them as a series. The precautions before referred to for preventing undue pressure, of course require especial attention in using mercury. This pressure, however, may be reduced to nothing after the mercury-tube is once filled, by keeping the level of the fluid the same, both in the vessel in which the gas is being received, and that into which the mercury driven out is being collected; for when the mercury-tube is filled, and its outside end dips into this vessel, it acts as a syphon. In order to do this, some additional mercury will of course be required. If, however, care be taken to make all the fittings tight, this will not be necessary, except in a very high apparatus.

VI.—*On the Law of Electrolysis.*

By Professor H. Buff.

The law of definite electrolytic decomposition, if not hitherto decidedly opposed, has yet been regarded as doubtful by many physicists. Others have considered it only as approximatively true; among those inclined to this view are Martius,* Schoenbein,† de la Rive,‡ &c. Jacobi, who as late as last year published some experiments on the electrolysis of sulphate of copper,§ is disposed to consider that the intensity of the action depends on the concentration of the solution. The celebrated discoverer of the electrolytic law has admitted, in the 12th series of his experimental researches on electricity, that fluid electrolytes may possibly conduct currents under a certain strength, without being decomposed by them; and that this conducting power, though not equal in different fluids capable of decomposition by electricity, yet in all cases obtains only in very weak currents.

As definite electric decomposition, if rigorously proved, presents a capital method of determining the unit of electricity, inasmuch as this unit would then become identical with the unit of chemical action, it appeared to me of great interest to ascertain by accurate measurements the limits between which the law of Faraday holds good. From the results of an investigation undertaken for this purpose, I consider it as proved, that even the smallest amount of electricity cannot pass through a liquid, capable of being decomposed, without producing an equivalent amount of decomposition.

According to the view generally adopted at present, I regard as electrolytes all chemical compounds which, like water, hydrochloric acid, chloride of lead, &c., consist of an electro-positive radical, which under galvanic influence collects at the negative electrode, and of an electro-negative radical, which is disengaged at the positive electrode. Thus sulphate of copper consists of the positive radical Cu and the negative one SO_4; nitrate of silver of the positive radical Ag and the negative NO_6; sulphate of ammonia of the positive radical NH_4

* Pogg. Ann. LVIII, 284; Inst. 1850, 30.
† Pogg. Ann. XLIII, 238.
‡ Pogg. Ann. LIV, 403.
§ Petersb. Acad. Bull. IX, 333.

and the negative one SO_4, &c. According to this view, the electrolytic action remains the same whether the current liberates an equivalent of hydrogen from water, or an equivalent of the radical NH_4 from a salt of ammonia. The question which I proposed to solve was, whether this action is only attendant on currents of certain strength, or whether it takes place proportionately with the weakest currents.

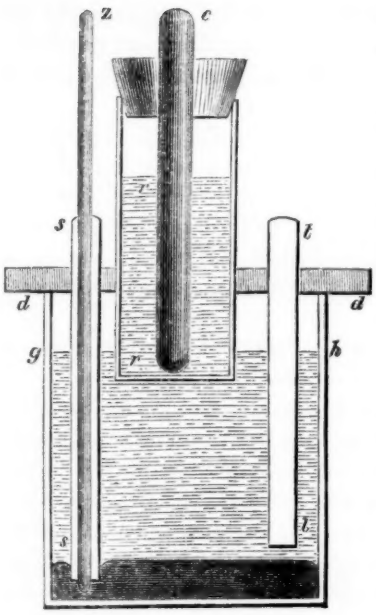
In order to apply very weak currents to electrolytic processes, and yet to separate a quantity of substance sufficient for weighing, it was necessary that a galvanic battery should be arranged as to give a weak but perfectly constant current, for some days at least. None of the known batteries answered this purpose. But as this want of uniform action in the so-called constant batteries arises more from deteriorating influences, than from the principle of their construction, I tried to obviate the former as much as possible, and I succeeded best by a modification of Daniell's battery. A little loss of power is produced in this battery by the zinc being gradually converted by the surrounding acid into sulphate of zinc.

This evil may, however, as is well known, be easily avoided by filling the zinc cell at once with sulphate of zinc. It is true that the resistance to conduction is increased in this way, but this is scarcely worth consideration with a current which has to traverse a long distance. The principal cause of variation in Daniell's battery when currents of long duration but small power are required, is caused by the copper solution gradually passing over by endosmosis into the zinc solution. Not only is copper precipitated chemically by this means, and consequently the equivalent amount of zinc lost for the process; but the copper precipitated on the surface of the zinc of course alters the state of the surface of the electro-positive metal, while it gives rise at the same time to secondary currents, which hasten the precipitation of copper and consequent loss of zinc.

These local currents are moreover the cause of the deposition of copper in the pores of the cells, and of its appearing even on the outer surface of the same.

By the following contrivance, of which the accompanying sketch represents a section, the influence of endosmosis was reduced to a minimum.

A glass vessel with ground edges is provided with a well-fitting cover *dd*, having three apertures, into which are introduced three glass tubes. The middle one *rr*, which should be as wide as possible, is closed at the lower end with bladder; of the two other tubes, *ss* and *tt*, the tube *ss* descends into a layer of mercury covering the



bottom of the vessel, while the other *tt* has its lower aperture at the sulphate of zinc, so that the liquid moistens the porous diaphragm of the tube *rr*. In this tube a solution of sulphate of copper, together with some crystals, is introduced. By introducing a strip of copper *c* into the tube *rr*, and a piece of zinc *z* into the tube *ss*, and connecting *c with z*, by means of a conductor, a perfectly constant current is produced, inasmuch as the mercury continually dissolves as much zinc as is necessary to keep up a steady action. Endosmosis is certainly not quite prevented by this arrangement; but it takes place very slowly, the zinc solution being more dense than that of the copper. As the lower extremity of the zinc is dissolved by the mercury, the rod gradually falls. In order to facilitate the renewal of the sulphate of copper, without deranging the current, the strip of copper is held in its place by a cork, which half fills the opening. The tube *tt* serves to remove from time to time a little sulphate of zinc by means of a pipette, and to replace what is removed by water. Batteries of this description have been in use since the middle of July, without their action having varied, up to the 1st of October, and without the necessity of disconnecting them; towards the middle of the latter month, a slight diminution of the current was perceptible. Upon closer examination, it was found to have arisen from a deposition of oxide of iron in the pores of the bladder, which was otherwise perfect.

Although this battery when in action presents a considerably greater resistance to conduction than the ordinary Daniell's battery, it is nevertheless well adapted for working the electric telegraph, and I have no doubt that, when once applied to this purpose, it will replace all other arrangements.

The advantages it possesses over the ordinary Daniell's battery may be easily seen from the following experiment. One element of the latter was connected with one wire of a galvanometer by means

of two wires of equal length. A deflection of 78° was produced on the galvanometer. A second element of the modified construction, when connected with the other wire of the galvanometer, caused a deflection of 77°·5.

When both currents were passed simultaneously, but in opposite directions, through the coil of the galvanometer, a deflection of 8°·5 was produced in favour of Daniell's battery. This decreased in two hours to 8°, in twenty hours to 7°·5, and continued constantly diminishing. After nine days, the Daniell's battery only caused a deflection of 33°, while that of the modified arrangement remained constant at 77°·5.

The equivalent of zinc electrolytically consumed for a current of this strength, during an action of 13085 minutes' duration, is 164·6 milligrammes. The actual amount consumed in the constant battery, however, was 1140 milligrammes, or 7 times that quantity, while in Daniell's battery, 27700 milligrammes, or 168 times the quantity of zinc were consumed. These great losses were occasioned by local actions, and would consequently appear less considerable with stronger currents. The constant battery described above has been exclusively used for the following experiments. One and the same pair served throughout the whole investigation, which lasted several months, without its being necessary to disconnect them once; nothing was done to them excepting that from time to time small pieces of sulphate of copper were added.

To determine the relation which the electrolytic action bears to the strength of current, I employed a neutral solution of nitrate of silver. In this were immersed two strips of chemically pure silver, so that under the influence of the battery, silver was dissolved from one strip, while it was deposited upon the other. For the pure metal, as well as for a perfectly pure and neutral solution of nitrate of silver, I am indebted to the kindness of Professor von Liebig, who prepared both himself expressly for this investigation. The alteration of the strength of the current was effected by interposing wires of various lengths. For this purpose I employed two copper wires, perfectly equal and very thin, of such a length that each presented a resistance to conduction equal to that caused by a silver wire of 1·5 millimetres in thickness and 1,800,000 metres in length. It is evident that, in comparison to such an immense resistance, that of the galvanic element, together with that of the decomposing cell, would form only a small fraction. Both were, however, specially measured, and it was found that together they only were equal to $\frac{1}{130}$th of that produced by the whole length of wire. According as the wires r and r

were introduced successively, or singly, or both together (representing a wire of double section) into the galvanic circuit, three currents were produced, the strength of which bore almost exactly the proportion of 1 : 2 : 4. The weight of silver electrically deposited bore the same proportion, as will be seen from the following table:

Resistance of the wire.	Duration of current.	Weight of deposited silver in milligrammes: Found.	Calculated for 6000 minutes.
$r+r'$	2547 minutes	55·5	130·74
r	1393 „	60·1	258·87
r'	1411 „	60·95	259·17
$\frac{r+r'}{4}$	720 „	62·2	518·33

The weakest current employed was capable of precipitating in 100 hours 130·74 milligrammes of silver. The equivalent amount of hydrogen is 1·2 milligrammes, or 13·42 cub. cent., which quantity would therefore have been liberated by the same current in 100 hours. This gas being somewhat soluble in water, as well as in acids and in solutions of salts, it is evident why the electrolysis of water by weak currents has escaped observation, and why some physicists have been led to believe that water can conduct small quantities of electricity without suffering decomposition.

In order to ascertain whether the decomposing power of weak currents is the same in different parts of the circuit, two cells filled with silver solution of the same composition were connected by the whole length of wire $r+r'$ with the constant battery. The current was passed with unvarying strength for nearly 9 days, or 12538 minutes. The following were the results:

1st. cell. Loss of weight of the positive silver strip = 267 mllgrms.
Gain of weight of the negative silver strip = 266·6 „
2nd. „ Loss of weight of the positive silver strip = 267·6 „
Gain of weight of the negative silver strip = 267·4 „

1 cub. cent. of the solution employed contained 25 milligrammes of neutral nitrate of silver.

To ascertain whether the state of concentration of the fluid had any influence, a more dilute solution was prepared, of which 1 cub. cent. contained 10 milligrammes of salt. Two cells filled with these solutions were introduced, together with the wire r, into the circuit. The experiment lasted 51·5 hours. After this time, the negative strip of silver in the stronger solution had gained 124·66 milligrammes in weight; while the corresponding strip in the more dilute solution had

gained 124·16 milligrammes. The state of dilution has therefore no influence on the results of the electrolysis.

To obtain comparative results, it is necessary that the solutions should be perfectly pure.

Less silver is apparently deposited from acid solutions than is required by the law, and in alkaline solutions of cyanide of silver, some of the precipitated silver is also redissolved.

When the weakest current was employed, that is, when the whole length of wire $r+r'$ was included, the amount of silver dissolved in 10 hours was greater than that deposited. Acid solutions of sulphate of copper likewise yield, on galvanic decomposition, too little copper; this is caused by the simultaneous action of the atmospheric oxygen and of the free acid on the negative copper plate.

When a galvanic current was passed at the same time through a perfectly pure neutral solution of sulphate of copper, and through a solution of nitrate of silver, the results of the electrolysis of these two solutions showed a close coincidence in the metals deposited. The following are a few of the numbers obtained:

Duration of experiment in minutes.	Amount of silver in milligrammes.	Amount of copper:		Strength of current.
		Found.	Calculated.	
2669	107·4	33·9	31·44	1·85
1236	534·5	157·9	156·5	19·88
1397	683·85	200·6	200·2	22·5
1029	535·7	157·6	156·82	24·5
458	862·4	257·8	252·5	86·6

The strength of the current produced when the whole length of wire $r+r'$ was introduced, has been assumed as the unit of strength. After each experiment was ended, the copper was deposited on a strip of platinum, was freed from adhering sulphate by washing with boiled water, and then dried *in vacuo* over concentrated sulphuric acid. It was always covered with a thin coating of suboxide, from which it was freed by ignition in a current of hydrogen. In order to prevent this oxidation of the copper as much as possible during the experiment, the solution was previously freed from air. Some decompositions were effected entirely under the air-pump. During the experiment, hydrogen was frequently passed through the solution; none of these precautions were however quite effectual. Even that copper which had been ignited in hydrogen, and was consequently perfectly pure, soon became covered with a thin film of oxide, sometimes even during the time occupied in weighing.

The facility with which galvanically deposited copper absorbs oxygen from the air, is the reason why in all cases a little more copper was obtained than corresponds to the equivalent of silver.

It would scarcely be possible to prove the law of definite electrolytic action with other bodies capable of galvanic decomposition as readily as with copper- or silver-salts. I consider myself however justified in concluding, from the foregoing experiments, that wherever deviations from the law have been observed, they have been caused by local actions, which, however, it may not always be possible to obviate.

VII.—*Analytical Notes.*

By A. B. Northcote and A. H. Church.

1. *On the Action of Caustic Potash on the Phosphates.*

Experiments were undertaken on this subject with the view of discovering a better method than that generally adopted for estimating phosphoric acid,—the results obtained when the iron precipitate suspected to contain phosphoric acid is dissolved in hydrochloric acid, the solution treated with tartaric acid and ammonia, and subsequently, a salt of magnesia added to precipitate the phosphoric acid, being frequently found to give erroneous conclusions, because the tartaric acid solution often produces a precipitate in magnesia-salts, probably of ammonio-tartrate of magnesia, without a trace of phosphoric acid being present.

It has hitherto been supposed that the phosphate of sesquioxide of iron is but imperfectly attacked by solutions of the caustic alkalies, but the extent of the decomposition which can be thus effected had not been submitted to a careful experimental inquiry.

From the authors' experiments it appears that by boiling the precipitate of iron with a sufficient excess of potash, the phosphoric acid is completely transferred to the latter base; this method of proceeding is therefore recommended in the quantitative determination of phosphoric acid. It is proposed that the alkaline solution be deprived of alumina which might be introduced with the potash, by the addition of silicate of potash, and subsequently of excess of hydrochloric acid and ammonia. The filtered solution will then contain the whole of the phosphoric acid, which may be readily precipitated by a salt of magnesia.

2. *On the behaviour of some Oxides with Caustic Potash in the presence of Oxide of Chromium.*

The influence of the association of sesquioxide of chromium with metallic oxides, which by themselves are insoluble in solution of caustic potash, is well known; the insoluble oxides being, in some cases, rendered soluble when thus associated, while in the other cases, they communicate their insolubility to the otherwise soluble oxide of chromium.

The object of the inquiry instituted with reference to these results was to ascertain the exact conditions under which complete solution or precipitation of the associated oxides occurs. It was found that complete solution takes place when the chromium, as sesquioxide, is associated with 40 per cent of iron, as sesquioxide, with 12·5 per cent of manganese, 20 per cent of cobalt, or 25 per cent of nickel, as protoxides; and that complete precipitation takes place when the chromium, as sesquioxide, is associated with 80 per cent of iron, 60 per cent of manganese, 50 per cent of cobalt, or 50 per cent of nickel, as protoxide. When cobalt and nickel, however, are thus rendered soluble, the result is not permanent; and ultimately, not only does the oxide of cobalt or nickel become insoluble, but it carries down with it some of the oxide of chromium.

The other metallic oxides soluble in caustic potash were not found to be influenced in their relations with caustic potash by the presence of sesquioxide of iron, or to exert any influence upon that oxide.

PROCEEDINGS

AT THE

MEETINGS OF THE CHEMICAL SOCIETY.

January 17, 1853.

Dr. Daubeny, President, in the Chair.

John Carty, Esq., of Bond Street, was duly elected a Fellow of the Society.

Dr. Miller described a new form of Pipette for transferring gases.

Dr. H. Bence Jones explained a new process which he has recently proposed for dissolving Calculi in the Bladder through the agency of Electricity.

February 7, 1853.

COLONEL PHILIP YORKE, Vice-President, in the Chair.

The following donations were announced:

"Denkschriften der kaiserlichen Akademie der Wissenschaften:" Vol. III, Parts 1 and 3.

"Sitzungsberichte der kaiserlichen Akademie der Wissenschaften:" Vol. VII, Parts 3, 4, and 5; and Vol. VIII, Parts 1, 2 and 3: from the Imperial Academy of Vienna.

"Berichte über die Mittheilungen von Freunden der Naturwissenschaften in Wien;" von Wilhelm Haidinger: VIIter and letzter Band.

"Naturwissenschaftlische Abhandlungen, gesammelt und durch Subscription herausgegeben;" von Wilhelm Haidinger: Vol. IV, in 4 Parts: from the Author.

"Abhandlungen der mathemat.-physikalischen Classe der königlich-bayerischen Akademie der Wissenchaften," Vol. VI, Parts 2 and 3; from the Royal Academy of Bavaria.

"Ueber die Siedepunkte mehrerer alkoholhaltiger Flüssigkeiten und die darauf gegründeten Verfahren, &c.," von J. J. Pohl.

"Nachtrag zur thermo-aräometrischen Bierprobe," von J. J. Pohl.

"Beitrag zur Statistik des Studiums der Chemie am k. k. polytechnischen Institute zu Wien:" von J. J. Pohl.

"Physikalish-chemische Notizen," von J. J. Pohl.

"Ueber die Zusammensetzung und Eigenschaften zweier Legierungen von Zinn und Blei," von J. J. Pohl.

"Ermittelung des technischen Werthes der Kartoffeln," von J. J. Pohl: from the Author.

"Barometrical Tables," by J. J. Pohl and J. Schabus.

"Calendar of the Flora of Prague during an observation of nearly ten years," by Karl Fritsch: from the Author.

"A new Theory of the Central Heat of the Earth, &c."

"On the Cause of the Phenomena exhibited by the Geysers of Iceland," and other pamphlets, by Stevenson Macadam: from the Author.

"Proceedings of the American Philosophical Society:" from the Society.

"The Journal of the Society of Arts:" from the Society.

Frank Clarke Hill, Esq., of the Chemical Works, Deptford;

Dr. Marcet, of 88, Cadogan Place; and J. J. Pohl, Esq., Professor of Applied Chemistry in the Polytechnic School of Vienna, were duly elected Fellows of the Society.

A paper was read:

"On the Mode of Estimating the Value of Red Prussiate of Potash, and of Testing the strength of Bleaching Liquors," by Francis Lieshing.

February 21, 1853.

DR. DAUBENY, President, in the Chair.

Alfred Coleman, Esq., Bridgefield, Wandsworth; John Gotch Hepburn, L.L.B., Clapham; Stevenson Macadam, Esq., Philosophical Institution, Edinburgh; and George Foord, Esq., Melbourne, were duly elected Fellows of the Society.

The President declared the names of the Officers and other Members of Council proposed by the Council to retire from Office, and of the Officers and other Members of Council proposed to be substituted for them at the ensuing Anniversary Meeting.

Mr. John Arthur Phillips made a communication on the subject of Ancient Metallurgy.

March 7, 1853.

PROFESSOR GRAHAM in the Chair.

Alfred Coleman, Esq., was admitted a Fellow of the Society. William Crowder, Esq., 21, Northumberland Street, Newcastle-on-Tyne; Dr. William Charles Henry, F.R.S., of Hatfield, near Ledbury; and Christopher R. James, Esq., of Ebbw Vale Iron Works, Abergavenny, were duly elected Fellows of the Society.

Mr. Redwood made a communication on the Optical Properties of the Alkaloids found in the Cinchona Barks, and on some facts recently elicited relating to the History of Racemic Acid.

March 21, 1853.

DR. DAUBENY, President, in the Chair.

H. Pollock, Esq., of Queen Square House, Guildford Street, was duly elected a Fellow of the Society.

Dr. Williamson made a communication on the Atomic Theory.

NOTICES

OF

PAPERS CONTAINED IN OTHER JOURNALS.

On a new series of Organic Bodies containing Metals.

By Dr. E. Frankland.

(From the "Philosophical Transactions," abstracted by the Author.)

Under the above title, I described more than three years ago some preliminary experiments,* which proved the existence of certain organic compounds highly analogous to cacodyl, and like that body, consisting of a metal, or in some cases of phosphorus, associated with the groups C_2H_3, C_4H_5, &c., and possessing, in some instances, highly remarkable powers of combination. I fixed the composition, and studied some of the reactions of two of these bodies, to which the names zinc-methyl (C_2H_3Zn) and zinc-ethyl (C_4H_5Zn), were provisionally assigned, besides giving methods for procuring similar compounds containing tin, arsenic and phosphorus, by acting upon the iodides of the alcohol-radicals with these elements, and expressing a belief, founded upon the similarity of functions existing between hydrogen and the groups of the form $C_nH_{(n+1)}$, that most, if not the whole, of the compounds contained in the following series might be formed, those marked thus * being at that time already known.

Hydrogen series.	Methyl series.	Ethyl series.	Butyl series.	Valyl series.	Amyl series.	Phenyl series.
ZnH	ZnC_2H_3*	ZnC_4H_5*	ZnC_6H_7	ZnC_8H_9	$ZnC_{10}H_{11}$	$ZnC_{12}H_5$
AsH_2*	$As(C_2H_3)_2$*	$As(C_4H_5)_2$	$As(C_6H_7)_2$	$As(C_8H_9)_2$	$As(C_{10}H_{11})_2$	$As(C_{12}H_5)_2$
SbH_3*	$Sb(C_2H_3)_3$	$Sb(C_4H_5)_3$	$Sb(C_6H_7)_3$	$Sb(C_8H_9)_3$	$Sb(C_{10}H_{11})_3$	$Sb(C_{12}H_{13})_3$
PH_3*	$P(C_2H_3)_3$*	$P(C_4H_5)_3$	$P(C_6H_7)_3$	$P(C_8H_9)_3$	$P(C_{10}H_{11})_3$	$P(C_{12}H_{13})_3$

More recently, Löwig and Schweitzer† have commenced labour-

* Ann. Ch. Pharm. LXXI, 213; Chem. Soc. Qu. J. II, 297.

† Ann. Ch. Pharm. LXXV, 315.

ing in the same field, and have filled up one of the gaps in the foregoing table by the formation of stibethyl, $Sb(C_4H_5)_3$, by acting upon iodide of ethyl with an alloy of antimony and potassium. The same chemists state, also, the probable formation of similar compounds containing methyl and amyl in the place of ethyl, and bismuth and phosphorus instead of antimony.

The agents which I have employed in the formation of these organo-metallic bodies are two—viz.: heat and light; in many cases, either of these can be used, in others, only one can be made to effect the desired combination, whilst more rarely the assistance of both appears to be essential. In those experiments in which heat was employed, the materials were subjected to its action in sealed glass tubes, about 12 inches long, and varying in diameter from $\frac{1}{2}$ inch to 1 inch, the thickness of the glass being about $\frac{1}{8}$ inch. To preserve the gaseous products of the operation in a state of perfect purity for subsequent investigation, the tubes were well exhausted before being sealed; they were then immersed to about half their depth in an oil-bath, and heated to the required temperature. In cases where the influence of light was employed, the materials, confined in tubes of precisely similar dimensions, were exposed to the sun's rays, concentrated in most instances by an 18-inch parabolic reflector, near the focus of which the tubes were placed, either naked, or surrounded by a solution of sulphate of copper, to absorb the calorific rays. By this arrangement, the light and heat could be increased, diminished, or modified, at pleasure, which was found very convenient in several of the operations.

ACTION OF TIN UPON IODIDE OF ETHYL.

When iodide of ethyl and metallic tin are exposed to the action of either heat or light, the tin gradually dissolves in the ethereal liquid, which finally solidifies to a mass of nearly colourless crystals. This reaction is effected most conveniently by the action of light, an excess of tin-foil, cut into narrow strips, being employed. The sealed tubes containing these ingredients should be placed near the focus of a large parabolic reflector, the temperature being prevented, if necessary, from rising too high, by immersing them in water, or in a solution of sulphate of copper. The unconcentrated rays of the sun, or even diffused daylight, are quite sufficient to determine the formation of the crystalline body; but an exposure of several weeks, or even months, would be necessary for the completion of the change which is effected by the use of the reflector in a few days of bright sunshine. The liquid gradually assumes a straw-yellow colour, but its solidification is prevented as long as possible at the close of the operation, by allowing the temperature to rise to 35°, or 40° C.; thus nearly the whole of the iodide of ethyl becomes

united with tin. When heat instead of light is employed to effect the combination, the tubes should not be more than ½ inch in diameter, and to avoid the risk of explosion, should only be one-fourth filled with the materials: the combination takes place at about 180° C. The agency of heat is, therefore, much less convenient than that of light in the production of this reaction, which is also never so complete as when the latter agent is employed. I have, however, satisfied myself that the results are the same in both cases.

I. *Examination of Solid Products.*—The capillary extremities of the tubes in which the foregoing reaction has taken place were broken off, under sulphuretted water, and beneath a jar filled with the same liquid:* the gases evolved were preserved for eudiometrical investigation. The crystalline product was then withdrawn from the tubes, and after being exposed to a gentle heat for a few minutes, to expel the iodide of ethyl that had escaped combination, was treated with alcohol, in which the crystals readily dissolved, leaving only a small residue of a bright red colour, which proved to be protoiodide of tin. The filtered alcoholic solution was then placed over sulphuric acid *in vacuo*, where it soon deposited a large crop of long, needle-like crystals, which, when freed from the mother-liquor, washed with a small quantity of dilute alcohol, dried between folds of bibulous-paper, and, finally, over sulphuric acid *in vacuo*, yielded analytical results corresponding closely with the formula:

$$C_4 H_5 Sn I.$$

This body is, therefore, the iodide of a new organo-metallic radical, for which I propose the name, STANETHYLIUM.

Iodide of Stanethylium crystallizes in transparent, slightly straw-coloured needles, which are right-rectangular prisms, frequently $\frac{1}{12}$ inch broad, and 2 or 3 inches in length. They are very soluble in ether and in boiling alcohol, less so in cold alcohol and in water; the watery solution is decomposed on boiling, oxide of stanethylium being precipitated, and hydriodic acid formed. Iodide of stanethylium fuses at 42° C., and boils at 240° C., undergoing, at the same time, partial decomposition; it possesses at common temperatures a peculiar pungent odour, somewhat resembling the volatile oil of mustard, and which irritates the eyes and lining membrane of the nose, causing a discharge, which continues for several hours, or even days, especially if the vapour from the heated iodide of stanethylium be inhaled; yet this compound can scarcely be said to be volatile at common temperatures, since a few grains may be exposed to the air for several weeks without any appreciable loss of weight.

Oxide of Stanethylium.—In contact with solutions of the alkalies, iodide of stanethylium is immediately decomposed, oxide of stanethylium and an alkaline iodide being formed:

* Chem. Soc. Qu. J. II, 267.

$$\left.\begin{matrix} C_4 H_5 Sn I \\ KO \end{matrix}\right\} = \left\{\begin{matrix} C_4 H_5 Sn O. \\ KI. \end{matrix}\right.$$

With solutions of potash and soda, the oxide of stanethylium dissolves in an excess of the precipitant, but is reprecipitated, unchanged, by cautious neutralization. The precipitated oxide is almost completely insoluble in an excess of ammonia. A quantity of the oxide of stanethylium, prepared by precipitation with an excess of ammonia, and submitted to analysis, yielded results agreeing with the above formula.

Oxide of stanethylium presents the appearance of a somewhat cream-white amorphous powder, closely resembling peroxide of tin, but less heavy than that oxide; it has a peculiar, though slight ethereal odour, and a bitter taste; it is insoluble in water, alcohol and ether, but readily dissolves in solutions of the acids, and of the fixed alkalies; with acids it forms salts, which are, however, for the most part difficultly crystallizable; those with strong acids exhibit an acid reaction. The nitrate deflagrates when heated to about 120° C., and on the application of a higher heat becomes pure peroxide of tin. The salts of the oxide of stanethylium behave with reagents so nearly like the salts of peroxide of tin, that the two are very difficult to distinguish from each other.

Sulphide of Stanethylium.—When sulphuretted hydrogen is passed through an acid solution of a salt of stanethylium, a cream-coloured precipitate falls, which is insoluble in dilute acids and ammonia, but soluble in concentrated hydrochloric acid, solutions of the fixed alkalies and alkaline sulphides; from its solutions in the fixed alkalies and alkaline sulphides it is reprecipitated unchanged on the addition of an acid. Its formula is $C_4 H_5 Sn S$, and it is produced by the following reaction:

$$\left.\begin{matrix} C_4 H_5 Sn O \\ HS \end{matrix}\right\} = \left\{\begin{matrix} C_4 H_5 Sn S \\ HO. \end{matrix}\right.$$

Sulphide of stanethylium presents the appearance of an amorphous cream-coloured powder, having a pungent and very nauseous smell, resembling that of decaying horseradish; when heated it fuses, froths up and decomposes, emitting vapours of a most insupportable odour. Heated with nitric acid it is decomposed, with the formation of peroxide of tin.

Chloride of Stanethylium, $C_4 H_5 Sn Cl$.—This salt is best prepared by dissolving oxide of stanethylium in dilute hydrochloric acid; on evaporation at a gentle heat or over sulphuric acid *in vacuo*, the chloride crystallizes out in long colourless needles, isomorphous with the iodide, which salt it also closely resembles in all its properties; it is, however, more volatile, and therefore emits a more intensely pungent and irritating odour than the iodide.

Stanethylium.—When a strip of zinc is immersed in a solution of

a salt of stanethylium (a solution of the chloride of stanethylium is the best for this purpose), it speedily becomes covered with dense oily drops of a yellow colour, which finally separate from the lower extremity of the zinc, and accumulate at the bottom of the vessel; the formation of the oily liquid is much favoured by gentle heat. The yellow oil, well washed with water, dried over chloride of calcium, and submitted to analysis, yielded results agreeing with the formula $C_4 H_5 Sn$, and showing that stanethylium is formed by the following simple reaction:

$$\left.\begin{matrix} C_4 H_5 Sn Cl \\ Zn \end{matrix}\right\} = \left\{\begin{matrix} C_4 H_5 Sn \\ Zn Cl. \end{matrix}\right.$$

Stanethylium is a thick, heavy, oily liquid, of a yellow or brownish-yellow colour and an exceedingly pungent odour, resembling that of its compounds, but much more powerful. It is insoluble in water, but soluble in alcohol and ether. At about 150° C. it enters into ebullition, a quantity of metallic tin is deposited, and a colourless liquid distils over, having a peculiar odour, containing a considerable quantity of tin and exhibiting no tendency to combine with iodine or bromine. I have not yet further examined this liquid; but it possibly consists of, or contains, *binethide of tin*, $Sn (C_4 H_5)_2$. In contact with air, stanethylium rapidly attracts oxygen, and is converted into a white powder, which has all the properties of oxide of stanethylium. Chloride, iodide and bromide of stanethylium, are instantaneously formed by the action of chlorine, iodine and bromine, or their hydrogen acids, respectively, upon stanethylium; the two first are in every respect identical with the salts above described, and the bromide, which closely resembles them, yielded analytical results in harmony with the formula

$$C_4 H_5 Sn Br.$$

Thus, stanethylium perfectly resembles cacodyl in its reactions, combining directly with the electro-negative elements, and regenerating the compounds from which it has been derived.

II. *Examination of Gaseous Products.*—The examination of the gases evolved on opening the tubes in which iodide of ethyl and tin had been exposed to the action of heat or light, showed that they consisted of hydride of ethyl and olefiant gas, in proportions indicated by the following percentage numbers:

	I. and II.	III.
Hydride of Ethyl. . .	81·61	81·43
Olefiant gas . . .	16·82	17·28
Nitrogen	1·57	1·29
	100·00	100·00

The presence of hydride of ethyl and olefiant gas, amongst the

products of the action of heat, or light, upon iodide of ethyl and tin, shows that the direct combination of these latter bodies is not the only reaction which takes place, but that a portion of the iodide of ethyl is also decomposed by the tin, with the production of iodide of tin and ethyl, the latter body being transformed, at the moment of its liberation, into hydride of ethyl and olefiant gas, a catalysis to which this radical is so prone.

$$\left.\begin{matrix} 2\,C_4H_5I \\ 2\,Sn \end{matrix}\right\} = \left\{\begin{matrix} C_4H_5, H \\ C_4H_4 \\ 2\,Sn\,I \end{matrix}\right.$$

The large excess of hydride of ethyl exhibited in the above analytical results, may have been caused, either by the greater solubility of olefiant gas in iodide of ethyl (a further and considerable amount of gas being expelled from the tubes by a gentle heat), or by the presence of moisture in the materials, which would give rise to the formation of oxyiodide of tin and hydride of ethyl.

$$\left.\begin{matrix} C_4H_5I \\ HO \\ 2\,Sn \end{matrix}\right\} = \left\{\begin{matrix} C_4H_5H \\ \\ SnO + SnI. \end{matrix}\right.$$

Both these causes probably contributed to produce the excess of hydride of ethyl; but the very small amount of gaseous products compared with the solid ones, shows that the production of the former is only an accidental circumstance, which, however it may be interpreted, does not at all affect the principal reaction—viz.: the formation of iodide of stanethylium.

$$\left.\begin{matrix} C_4H_5I \\ Sn \end{matrix}\right\} = C_4H_5SnI.$$

STANMETHYLIUM and STANAMYLIUM, are formed when the iodides of methyl and amyl, respectively, are exposed to the action of light in contact with tin. Their salts are isomorphous with those of stanethylium; but I have not completed the investigation of these bodies.

ACTION OF ZINC UPON IODIDE OF METHYL.

When iodide of methyl and zinc are exposed to a temperature of about 150° C., in a sealed tube, the zinc gradually dissolves, with the evolution of gas, whilst a mass of white crystals, and a colourless mobile liquid occupy, after a few hours, the place of the original materials. The gas evolved on breaking off the capillary extremity of the previously exhausted tube, was collected and preserved over sulphuretted water. I will refer to this gas again, under the name of α. On cutting off the upper portion of the tube, and pouring cold distilled water upon the mobile liquid and white mass of crystals just mentioned, a very violent action ensued, and a column of flame,

several feet high, shot up momentarily from the mouth of the tube; but the action soon became more moderate, and a cork and gas-delivering tube being fitted into the decomposition-tube, the gas was collected and preserved. I will call this second gas β.

Zincmethylium.—From a preliminary experiment, it was ascertained that the gas evolved on opening the decomposition-tube possessed, before contact with water, a most insupportable and very peculiar odour, and that when ignited it burnt with a greenish-blue flame, producing dense white fumes; when a porcelain plate was held in this flame, it immediately became coated with a jet-black deposit, surrounded with a white ring; this black deposit dissolved in dilute hydrochloric acid, with evolution of hydrogen gas, and the solution was found to contain chloride of zinc. Hence, it was evident that a gaseous, or volatile compound of zinc, was present amongst the products of decomposition, and this was soon found to reside in the mobile liquid above mentioned; for on inverting the tube, and allowing a few drops of the liquid to escape, it inflamed spontaneously the instant it came in contact with the air, and produced by its combustion large quantities of oxide of zinc. In order to obtain this liquid in a state of purity, another tube was charged with iodide of methyl and excess of zinc, and subjected to a heat of 150° to 160° C., until every trace of iodide of methyl was decomposed. The drawn-out extremity of the tube being broken off, the included gas was allowed to escape, and the liquid contents were then separated from the solid ones by distillation at a gentle heat, in an atmosphere of dry hydrogen. The analytical operations upon this liquid proved it to be a new radical, for which zincmethylium (C_2H_3Zn) will be a convenient name, and that it is formed by the following reaction:

$$\left.\begin{matrix} C_2H_3I \\ 2\,Zn \end{matrix}\right\} = \left\{\begin{matrix} C_2H_3Zn \\ ZnI. \end{matrix}\right.$$

Zincmethylium is a colourless, transparent and very mobile liquid, refracting light strongly, and possessing a peculiar, penetrating and insupportable odour; it is very volatile, but I have not yet been able to determine its boiling-point with accuracy. Zincmethylium combines directly with oxygen, chlorine, iodine, &c., forming somewhat unstable compounds, a description of which I reserve for a future communication. Its affinity for oxygen is even more intense than that of potassium; in contact with atmospheric air it instantaneously ignites, burning with a beautiful greenish-blue flame, and forming white clouds of oxide of zinc; in contact with pure oxygen, it burns with explosion, and the presence of a small quantity of its vapour in combustible gases, gives them the property of spontaneous inflammability in oxygen. Thrown into water, zincmethylium decomposes that liquid with explosive violence, and with the evolution of heat

and light; when the action is moderated, the sole products of the decomposition are oxide of zinc and hydride of methyl.

$$\left.\begin{matrix} C_2H_3Zn \\ HO \end{matrix}\right\} = \left\{\begin{matrix} C_2H_3H \\ ZnO. \end{matrix}\right.$$

The extraordinary affinity of zincmethylium for oxygen and electro-negative elements in general, its peculiar composition, and the facility with which it can be procured, cannot fail to cause its employment for a great variety of transformations in organic compounds. By its agency, there is every probability that we shall be able to replace oxygen, chlorine, &c., atom for atom, by methyl, and thus produce an entirely new series of organic compounds, and obtain clearer views of the constitution of others. I intend to pursue this branch of the subject whilst studying the compounds of zincmethylium, and the corresponding bodies containing ethyl and amyl.

An examination of the gas α, proved it to consist of equal volumes of methyl (C_2H_3), and hydride of methyl (C_2H_3, H): no trace of the first term of the olefiant gas series (C_2H_2) was present, although the analogous decomposition of the iodides of ethyl and amyl by zinc,* led me to search very carefully for it. The occurrence of methyl amongst the products of the decomposition shows that a portion of the iodide of methyl is decomposed, according to the following equation:

$$\left.\begin{matrix} C_2H_3I \\ Zn \end{matrix}\right\} = \left\{\begin{matrix} C_2H_3 \\ ZnI. \end{matrix}\right.$$

The origin of the hydride of methyl is readily perceived, when the volatility of zincmethylium, and the method of collecting the gas, are taken into consideration. On opening the decomposition-tube beneath water, a copious effervescence was observed wherever the evolved gas came in contact with water; and as this effervescence was accompanied by the formation of a flocculent precipitate of oxide of zinc, it could only be caused by the presence of the vapour of zincmethylium, which, on coming in contact with water, would be instantaneously decomposed into oxide of zinc and hydride of methyl.

The gas β, evolved by the action of water upon the solid and liquid products of the decomposition, was found, as might have been anticipated, to be pure hydride of methyl, derived from the decomposition of the zincmethylium, with which the crystalline residue of iodide of zinc was saturated.

Zincethylium (C_4H_5Zn) and Zincamylium ($C_{10}H_{11}Zn$), are formed under precisely similar circumstances, the iodides of ethyl and amyl being respectively substituted for iodide of methyl. They are colourless and transparent liquids, refracting light strongly, and

* Chem. Soc. Qu. J. II, 265; III, 30.

possessing a peculiar penetrating odour. They are less volatile than zincmethylium, and are also somewhat weaker in their powers of combination. They unite directly with oxygen, chlorine, &c., and are decomposed in contact with water in a manner perfectly analogous to zincmethylium, producing oxide of zinc, and the hydrides of ethyl and amyl, respectively.

ACTION OF MERCURY UPON IODIDE OF METHYL.

When iodide of methyl is exposed to sunlight, in contact with metallic mercury, it soon becomes coloured red, from the separation of free iodine; after several hours' exposure, this coloration disappears, and a small quantity of the yellow iodide of mercury subsides to the bottom of the liquid. After the action of sunlight for several days, the bulk of the mercury is observed to have considerably diminished; white crystals begin to be deposited around the sides of the glass vessel; and, finally, after about a week's exposure, the liquid solidifies to a colourless, crystalline mass; when this is digested with ether, the new compound dissolves, and is thus separated from metallic mercury and a small quantity of iodide of mercury, which is collaterally formed. Only a very small quantity of gas is evolved during the formation of this white crystalline compound. By spontaneous evaporation, the ethereal solution solidifies to a mass of minute, colourless, crystalline scales; these, dried *in vacuo*, and submitted to analysis, yielded results closely corresponding with the formula $C_2 H_3 Hg I$.

This compound is, therefore, evidently the iodide of a new organometallic radical, consisting of one atom of methyl and one atom of mercury, and for which I propose the name HYDRARGYROMETHYLIUM: its iodide is formed by the direct union of one atom of mercury with one atom of iodide of methyl, under the influence of light.

$$\left.\begin{matrix} C_2 H_3 I \\ Hg \end{matrix}\right\} = C_2 H_3 Hg I.$$

Iodide of hydrargyromethylium is a white solid, crystallizing in minute nacreous scales, which are insoluble in water, moderately soluble in alcohol, and very soluble in ether and iodide of methyl; by the spontaneous evaporation of these solutions, the crystals are again deposited unchanged. Iodide of hydrargyromethylium is slightly volatile at ordinary temperatures, and exhales a slight, but peculiarly unpleasant odour, which leaves a nauseous taste upon the palate for several days; at 100° C. the volatility is much greater, and the crystals are rapidly dissipated at this temperature, when exposed to a current of air. At 143° C. it fuses, and sublimes without decomposition, condensing in brilliant and extremely thin crystalline plates. In contact with solutions of the fixed alkalies and ammonia,

it is converted into oxide of hydrargyromethylium, which is dissolved in excess of all these reagents; from these solutions, sulphide of ammonium throws down sulphide of hydrargyromethylium as a slightly yellow, flocculent precipitate, having a most insupportable odour. I have not yet further examined the reactions of this remarkable body, nor have I attempted the isolation of the hydrargyromethylium.

A corresponding compound containing amyl is formed, though with difficulty, under similar circumstances; but I have not yet succeeded in producing one containing ethyl, the iodide of this radical yielding, as I have shown,* when exposed to sunlight in contact with mercury, iodide of mercury, and a mixture of ethyl, hydride of ethyl and olefiant gases.

I have also made some preliminary experiments with other metals, and find that most of them are capable of thus entering into combination with the organic groups, methyl, ethyl and amyl: amongst those which thus combine under the influence of light most readily, and seem to promise the most interesting results, I may mention, arsenic, antimony, chromium, iron, manganese and cadmium.

Imperfect as our knowledge of the organo-metallic bodies may yet appear, I am unwilling to close this memoir without directing attention to some peculiarities in the habits of these compounds, which promise, at least, to throw some light upon their rational constitution, if they do not lead to extensive modifications of our views respecting chemical compounds in general, and especially that interesting class termed conjugate compounds.

That stanethylium, zincmethylium, hydrargyromethylium, &c., are perfectly analogous to cacodyl, there can be no reasonable doubt, inasmuch as, like that body, they combine directly with the electronegative metalloids, forming true salts, from which in most cases, and probably in all, the original groups can be again separated unaltered; and, therefore, any view which may be taken of the new bodies must necessarily be extended to cacodyl. The discovery and isolation of this so-called organic radical by Bunsen, was certainly one of the most important steps in the development of organic chemistry, and one, the influence of which upon our theoretical views of the constitution of certain classes of organic compounds, can scarcely be too highly estimated. It was impossible to consider the striking features in the behaviour of this body, without finding in them a most remarkable confirmation of the theory of compound radicals, as propounded by Berzelius and Liebig.

The formation of cacodyl, its habits, and the products of its

* Chem. Soc. Qu. J. III, 331.

decomposition, have for some time left no doubt of the existence of methyl ready formed in this body; and Kolbe,* in developing his views on the so-called conjugate compounds, has proposed to regard it as arsenic conjugated with two atoms of methyl, $(C_2H_3)_2As$. So long as cacodyl was an isolated example of an organo-metallic body, this view of its rational composition, harmonizing as it did so well with the facts elicited during the route of cacodyl through its various combinations and decompositions, could scarcely be contested; but now, since we have become acquainted with the properties and reactions of a considerable number of analogous bodies, circumstances arise which I consider militate greatly against this view, if they do not render it absolutely untenable. According to the theory of conjugate radicals just alluded to, cacodyl and its congeners, so far as they are at present known, would be thus represented:

Cacodyl	$(C_2H_3)_2As$
Oxide of cacodyl	$(C_2H_3)_2AsO$
Cacodylic acid	$(C_2H_3)_2AsO_3$
Stanmethylium	$(C_2H_3)Sn$
Stanethylium	$(C_4H_5)Sn$
Oxide of stanethylium	$(C_4H_5)SnO$
Stanamylium	$(C_{10}H_{11})Sn$
Zincmethylium	$(C_2H_3)Zn$
Zincethylium	$(C_4H_5)Zn$
Zincamylium	$(C_{10}H_{11})Zn$
Stibethine (Stibethyl)	$(C_4H_5)_3Sb$
Binoxide of stibethine	$(C_4H_5)_3SbO_2$
Oxide of stibmethylium	$(C_2H_3)_4SbO$
Hydrargyromethylium	$(C_2H_3)Hg$
Iodide of hydrargyromethylium	$(C_2H_3)HgI$

It is generally admitted, that when a body becomes conjugated, its essential chemical character is not altered by the presence of the conjunct; thus, the series of acids $C_nH_nO_4$, formed by the conjunction of the radicals $C_nH_{(n+1)}$ with oxalic acid, have the same neutralizing power as the original oxalic acid, and, therefore, if we assume the organo-metallic bodies to be metals conjugated with various hydrocarbons, we might reasonably expect that the chemical relations of the metal to oxygen, chlorine, sulphur, &c., would remain unchanged. A glance at the formulæ of these compounds will, however, suffice to show that this is far from being the case. It is true, that cacodyl forms protoxide of cacodyl and cacodylic acid, corresponding, the one, to a somewhat hypothetical protoxide of arsenic, which, if it exist, does not seem to possess any well-defined

* Chem. Soc. Qu. J. III, 372.

basic character, and the other, to arsenious acid; but no compound corresponding to arsenic acid can be formed; and yet it cannot be urged that cacodylic acid is decomposed by the powerful reagents requisite to produce further oxidation, for concentrated nitric acid may be distilled from cacodylic acid without decomposition or oxidation, in the slightest degree. The same anomaly presents itself even more strikingly in the case of stanmethylium, which, if we are to regard it as a conjugate radical, ought to combine with oxygen in two proportions at least, to form compounds corresponding to protoxide and peroxide of tin. Stanethylium rapidly oxidizes when exposed to the air, and is converted into pure protoxide; but this compound exhibits none of that powerful tendency to combine with an additional equivalent of oxygen, which is so characteristic of protoxide of tin; nay, it may even be boiled with dilute nitric acid, without evincing any signs of oxidation. I have been quite unable to form any higher oxide than that described above: it is only when the group is entirely broken up, and the ethyl separated, that the tin can be induced to unite with another equivalent of oxygen. Stibethyl also refuses to unite with more or less than two equivalents of oxygen, sulphur, iodine, &c., and thus forms compounds, which are not at all represented amongst the combinations of the simple metal, antimony.

When the formulæ of inorganic chemical compounds are considered, even a superficial observer is struck with the great symmetry of their construction; the compounds of nitrogen, phosphorus, antimony and arsenic especially exhibit the tendency of these elements to form compounds containing three or five equivalents of other elements, and it is in these proportions that their affinities are best satisfied; thus in the ternal group we have NO_3, NH_3, NI_3, NS_3, PO_3, PH_3, PCl_3, $Sb\,O_3$, $Sb\,H_3$, $Sb\,Cl_3$, $As\,O_3$, $As\,H_3$, $As\,Cl_3$, &c., and in the five-atom group NO_5, NH_4O, $NH_4\,I$, PO_5, $PH_4\,I$, &c. Without offering any hypothesis regarding the cause of this symmetrical grouping of atoms, it is sufficiently evident, from the examples just given, that such a tendency or law prevails, and that, no matter what the character of the uniting atoms may be, the combining power of the attracting element, if I may be allowed the term, is always satisfied by the same number of these atoms. It was probably a glimpse of the operation of this law amongst the more complex organic groups which led Laurent and Dumas to the enunciation of the theory of types; and had not those distinguished chemists extended their views beyond the point to which they were well supported by then existing facts, had they not assumed that the properties of an organic compound are dependant upon the position, and not upon the nature of its single atoms, that theory would undoubtedly have contributed to the development of the science to a still greater extent than it has already done. Such an assumption could only have been made at a time

when the data upon which it was founded were few and imperfect, and as the study of the phenomena of substitution progressed it gradually become untenable, and the fundamental principles of the electro-chemical theory again assumed their sway. The formation and examination of the organo-metallic bodies promises to assist in effecting a fusion of the two theories which have so long divided the opinions of chemists, and which have too hastily been conceived irreconcileable; for whilst it is evident that certain types of series of compounds exist, it is equally clear that the nature of the body derived from the original type is essentially dependent upon the electro-chemical character of its chemical atoms, and not merely upon the relative position of those atoms. Let us examine, for instance, the compounds formed by zinc and antimony: by combination with one equivalent of oxygen, the electro-negative quality of the zinc is nearly annihilated, and it is only by the highly oxidizing peroxide of hydrogen that the metal can be made to form a very instable peroxide; but when zinc combines with one equivalent of methyl or ethyl, its positive quality, so far from being neutralized, is exalted by the addition of the positive group, and the compound now exhibits such intense affinity for the electro-negative elements as to give it the property of spontaneous inflammability. Peroxide of antimony has also little tendency to pass into a higher state of oxidation; but when its three atoms of oxygen are replaced by the electro-positive ethyl, as in stibethine, that affinity is elevated to the intense degree which is so remarkable in this body.

Taking this view of the so-called conjugate organic radicals, and regarding the oxygen, sulphur and chlorine compounds of each metal as the true molecular type of the organo-metallic bodies derived from it by the substitution of an organic group for oxygen, sulphur, &c., the anomalies above mentioned entirely disappear, and we have the following inorganic types and organo-metallic derivatives:

Inorganic types.		Organo-metallic derivatives.	
$As\{^{S}_{S}$	. . . .	$As\{^{C_2H_3}_{C_2H_3}$	Cacodyl.
$As\{^{O}_{O}_{O}$	. . . .	$As\{^{C_2H_3}_{C_2H_3}_{O}$	Oxide of Cacodyl.
$As\{^{O}_{O}_{O}_{O}_{O}$	. . . .	$As\{^{C_2H_3}_{C_2H_3}_{O}_{O}_{O}$	Cacodylic Acid.
$Zn\ O$	. . . .	$Zn\ (C_2H_3)$	Zincmethylium.
$Zn\{^{O}_{O}$	. . . .	$Zn\{^{C_2H_3}_{O}$	Oxide of Zincmethylium.

Inorganic types.		Organo-metallic derivatives.	
$Sb\left\{\begin{matrix}O\\O\\O\end{matrix}\right.$	. . . .	$Zn\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right.$	Stibethine.
$Sb\left\{\begin{matrix}O\\O\\O\\O\\O\end{matrix}\right.$	. . . .	$Sb\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\O\\O\end{matrix}\right.$	Binoxide of Stibethine.
$Sb\left\{\begin{matrix}O\\O\\O\\O\\O\end{matrix}\right.$	. . . .	$Sb\left\{\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\\O\end{matrix}\right.$	Oxide of Stibethylium.
Sn O	. . . .	Sn (C_4H_5)	Stanethylium.
$Sn\left\{\begin{matrix}O\\O\end{matrix}\right.$	. . . .	$Sn\left\{\begin{matrix}C_4H_5\\O\end{matrix}\right.$	Oxide of Stanethylium.
$Hg\left\{\begin{matrix}I\\I\end{matrix}\right.$	. . . .	$Hg\left\{\begin{matrix}C_2H_3\\I\end{matrix}\right.$	Iodide of Hydragyromethylium.

The only compound which does not harmonize with this view is ethostibilic acid, to which Löwig assigns the formula $C_4H_5SbO_5$; but as that chemist has not yet fully investigated this compound, it is possible that further research may satisfactorily elucidate its apparently anomalous composition.

It is obvious that the establishment of this view of the constitution of the organo-metallic bodies will remove them from the class of organic radicals and place them in intimate connection with ammonia and the bases of Wurtz, Hofmann, and Paul Thenard; indeed the close analogy existing between stibethine and ammonia, first suggested by Gerhardt, has been most satisfactorily demonstrated by the behaviour of stibethine with the haloid compounds of methyl and ethyl. Stibethine furnishes us therefore with a remarkable example of the law of symmetrical combination above alluded to, and shows that the formation of a five-atom group from one containing three atoms can be effected by the assimilation of two atoms, either of the same or of opposite electro-chemical character; this remarkable circumstance suggests the following question. Is this behaviour common also to the corresponding compounds of arsenic, phosphorus, and nitrogen; and can the position of each of the five atoms, with which these elements respectively combine, be occupied indifferently by an electro-negative or an electro-positive element? This question, so important for the advance of our knowledge of the organic bases and their congeners, cannot now long remain unanswered.

If the views which I have just ventured to suggest should be as

well supported by future researches as they are by the facts already known, they must occasion a profound change in the nomenclature of the extensive series of compounds affected by them. I have not, however, ventured to introduce this new system of nomenclature even in the case of the new bodies described in this memoir; since hasty changes of this kind, unless absolutely necessary, are always to be deplored. In accordance with the suggested view of the constitution of the organo-metalic compounds, the following plan of nomenclature would probably be found most convenient.

ARSENIC COMPOUNDS.

$(C_2 H_3)_2 As$ . . Bimethide of Arsenic (Cacodyl).
$(C_2 H_3)_2 AsO$ . . Bimethoxide of Arsenic (Oxide of Cacodyl).
$(C_2 H_3)_2 AsO_3$ . . Bimetharsenic Acid (Cacodylic Acid).

ZINC COMPOUNDS.

$(C_2 H_3) Zn$ . . Methide of Zinc (Zincmethylium).
$(C_4 H_5) Zn$ . . Ethide of Zinc (Zincethylium).
$(C_{10} H_{11}) Zn$ . . Amylide of Zinc (Zincamylium).

TIN COMPOUNDS.

$(C_2 H_3) Sn$ . . Methide of Tin (Stanmethylium).
$(C_2 H_3) SnI$ . . Methiodide of Tin (Iodide of Stanmethylium).
$(C_4 H_5) SnO$ . . Ethoxide of Tin (Oxide of Stanethylium).
$(C_{10} H_{11}) SnCl$ . . Amylochloride of Tin (Chloride of Stanamylium).

ANTIMONY COMPOUNDS.

$(C_2 H_3)_3 Sb$. Termethide of Antimony (Stibmethine).
$(C_2 H_3)_4 SbO$ . . Quadromethoxide of Antimony (Oxide of Stibmethylium).
$(C_4 H_5)_3 SbO_2$ . . Terethobinoxide of Antimony (Binoxide of Stibethine).

MERCURY COMPOUNDS.

$(C_2 H_3) Hg$ . . Methide of Mercury (Hydrargyromethylium).
$(C_2 H_3) HgI$ . . Methiodide of Mercury (Iodide of Hydrargyromethylium).

In naming the new bodies described in the present paper, I have, in conformity with the nomenclature of the organic bases, adopted the principle of employing the termination "*ium*," when the body unites with one equivalent of oxygen, chlorine, &c., like ammonium, and the terminal "*ine*," when like ammonia it combines with two additional atoms.

On Meconic Acid and its Derivatives.

By Henry How.*

This investigation was undertaken with the view of determining whether compounds analogous to those already described by the author† as derived from comenic acid, could be obtained under similar circumstances from meconic acid.

To obtain pure meconic acid, the crude acid—prepared by treating meconate of lime three times in succession with 20 parts of boiling water and 3 parts of strong hydrochloric acid—is mixed with about twice its weight of water, and heated over the water-bath with constant agitation, and caustic ammonia added till the whole is dissolved; the ammoniacal salt thus formed is very soluble in boiling water, and solidifies on cooling. The solid mass is subjected to strong pressure to remove the mother-liquid, and purified by three crystallizations from the smallest possible quantity of boiling water, the mother-liquor being expressed at each crystallization. The product is a perfectly white salt, from the solution of which in hot water, the meconic acid may be separated by hydrochloric acid in colourless shining laminæ; and on washing the precipitate a little with cold water, and dissolving in the smallest possible quantity of boiling water, the solution on cooling yields the acid in a state of perfect purity.

Bibasic Meconate of Ammonia.—The salt whose preparation has just been described, crystallizes from moderately dilute solutions, after standing, in radiated groups of fine silky needles, having an acid reaction. The salt dried at 100° has the composition :

$$HO, 2NH_4O . C_{14} HO_{11}.$$

It is very hygroscopic. The crystals appear to contain variable quantities of water of crystallization. An aqueous solution of this salt may be boiled without change; but when kept boiling for some time with an excess of ammonia, it becomes altered.

Action of Heat on Meconate of Ammonia.—Comenamic Acid.—Some of the highly coloured mother-liquors of the purifying process were retained at or near the boiling temperature, ammonia being present in excess, and hydrochloric acid added after cooling. Carbonic acid was then copiously evolved, and a considerable precipitate formed, consisting of comenamic acid, $C_{12} H_5 NO_8$, which, by repeated crystallization from boiling water, and the use of animal charcoal, was obtained in colourless shining scales. Its formation from bibasic meconate of ammonia may be represented by the following equation :

$$HO . 2NH_4O . C_{14} H . O_{11} = C_{12} H_5 NO_8 + NH_3 + 2HO + 2CO_2.$$

* Edinb. Phil. Trans. XX, Pt. III, 401 ; Ann. Ch. Pharm. LXXXIII, 350.
† Chem. Soc. Qu. J. IV, 362.

This reaction offers a convenient source of comenamic acid, as very impure meconic acid may be used.

Action of Chlorine on Bibasic Meconate of Ammonia.—Chlorine passed through the coloured mother-liquor deprives it of colour considerably, and causes a deposit of hard granular crystals, which may be purified by recrystallization from boiling water. Hard crystals are then deposited, which when magnified appear to consist of thick needles radiating from a centre. The salt thus formed contains no chlorine, but is a *monobasic meconate of ammonia*, $2HO \cdot NH_4O \cdot C_{14}HO_{11}$. The crystals likewise contain 7·70 per cent of water of crystallization $=2Aq$.

The original mother-liquor of this salt deposited a further quantity of the same on being concentrated, but by continued evaporation crystals of a different character were obtained; and these, when recrystallized from boiling water, presented themselves in the form of square prismatic needles, having the properties and composition of *chlorocomenic acid*, $2HO \cdot C_{12}\left\{\begin{matrix}H\\Cl\end{matrix}\right\}O_8$ The last mother-liquors of this process contain oxalic acid.

Action of Bromine on Meconic Acid.—When bromine-water is poured upon powdered meconic acid, carbonic acid is evolved with lively effervescence, and the acid dissolves, forming a solution which, after a while, deposits long prismatic crystals of great beauty; a much more copious product is however obtained by gentle evaporation. By recrystallization from hot water, brilliant square prismatic crystals are obtained, which when dried at 100° C. have the composition of dry bromocomenic acid, $2HO \cdot C_{12}\left\{\begin{matrix}H\\Br\end{matrix}\right\}O_8$. The nature of the reaction is shown by the equation:

$$C_{14}H_4O_{14}+2Br=C_{12}\left\{\begin{matrix}H\\Br\end{matrix}\right\}O_8+HBr+2CO_2+2HO$$

Crystals of oxalic acid were obtained by evaporating the mother-liquors to a small bulk.

The action of bromine on meconate of ammonia would doubtless be found similar to that of chlorine.

Ethers of Meconic Acid.—When a current of dry hydrochloric acid gas is passed through an alcoholic solution of meconic acid till it fumes strongly, and the liquid is set aside to cool, there appears, after a time, shorter or longer as the alcohol is stronger or weaker, a deposit of feathery crystals. If absolute alcohol has been used, the filtered liquid yields no further deposit; but if rectified spirit has been used, another less crystalline substance appears after a time.

On evaporating the liquid which has ceased to give deposits, to complete dryness, the chief constituent of the residue is found to be a substance which fuses under boiling water. It is more or less accompanied by the other bodies, according to the strength of the alcohol used.

Ethylomeconic Acid.—This is the first deposit above mentioned; it is formed most abundantly and in the state of greatest purity when absolute alcohol is used. One crystallization from hot water is sufficient to render it perfectly pure and uniform, and it then crystallizes in brilliant short needles. It is composed of $C_{18}H_8O_{14}$, and is an acid ether analogous to phosphovinic ether, its rational formula being,

$$2\,HO.C_4H_5O.C_{14}HO_{11}, \text{ or } \left.\begin{matrix} C_4H_5 \\ H \\ H \end{matrix}\right\} C_{14}HO_{14}$$

Ethylomeconic acid, when pure, crystallizes from boiling water, in which it is very soluble, in brilliant small crystals, which, when magnified, are seen to be square prismatic needles. It likewise dissolves readily in ether and common alcohol when warmed, less readily in absolute alcohol. It separates from concentrated solutions in these three liquids in groups of stellate crystals, and when left to spontaneous evaporation, in long needles. It is anhydrous; its crystals lose no weight either *in vacuo* or at 100° C. It fuses at about 158°—159° C. to a transparent yellowish liquid, a sublimate of very brilliant rhombic crystals being formed at the same time. The aqueous solution has a strongly acid reaction, imparts a deep-red colour to persalts of iron, and decomposes carbonates with effervescence. It is bibasic, forming two series of salts; the acid salts are readily crystallizable. Its salts are very stable, the acid being recoverable from them by decomposition with stronger acids.

Acid Ethylomeconate of Baryta, $BaO.HO.C_4H_5O.C_{14}HO_{11}$, is formed on adding carbonate of baryta in successive small portions to water covering solid ethylomeconic acid. Lively effervescence ensues, and the acid quickly disappears, a small quantity of an insoluble yellow salt being formed at the same time. If the liquid be filtered as soon as the effervescence ceases, and the vessel be placed *in vacuo*, a considerable quantity of carbonate of lime previously held in solution by the carbonic acid is deposited. By a second filtration, a clear, yellowish liquid is obtained, which, when evaporated *in vacuo*, or at a gentle heat, yields well-defined, brilliant, rhombic crystals of a yellow colour. The crystals contain water, which they lose on drying.

Acid Ethylomeconate of Silver, $AgO.HO.C_4H_5O.C_{14}HO_{11}$.—Obtained by adding an aqueous solution of the baryta-salt to nitrate of silver, dissolving the washed precipitate in boiling water, and crystallizing. Forms groups of fine, small, stellate crystals, brilliant

and white. It is remarkably stable, remaining perfectly unchanged when exposed for a long time to the diffused daylight of summer. The crystals contain 2 atoms water, which they give off at 100° C.

An aqueous solution of acid ethylomeconate of baryta forms wit acetate of lead a yellowish-white, with sulphate of copper a pale green, and with perchloride of iron a red-brown precipitate; the last is readily soluble in an excess of the iron-salt, forming with it a dark red liquid.

Neutral Salts of Ethylomeconic Acid.—These salts have not yet been obtained quite pure. By saturating ethylomeconic acid with carbonate of baryta at 100° C. and filtering, a salt was obtained in small, short, yellow needles, which, when dried at 100°, yielded 41·89 per cent baryta. The formula, $BaO . C_4 H_5 O . C_{14} HO_{11}$, requires 42·19. The salts obtained by treating the acid with excess of carbonate of baryta were found to contain from 42 to 44·5 per cent baryta; whence it would appear that the acid forms basic in addition to neutral and acid salts. Similar results were obtained with the other alkaline earths. The acid, when heated with excess of carbonate of silver, remains almost wholly undissolved in the form of some basic compound; heated with excess of potash or soda, it yields *meconates* of these bases. An excess of caustic ammonia decomposes it very readily.

Meconamidic Acid.—When ethylomeconic acid is dissolved in warm water or alcohol, and an excess of strong aqueous or alcoholic ammonia is added, the liquid assumes a deep-yellow colour, and becomes very soon filled with a yellow, semi-gelatinous substance, which, after being washed with dilute spirit, dries up in the air to an amorphous mass, reducible with some difficulty to a very fine yellow powder. It appears to be the ammonia-salt of a peculiar acid; for, on treating its solution in hot water with hydrochloric acid, a white precipitate is formed, which, on being recrystallized from boiling water, is found to have the composition, $C_{84} H_{39} N_7 O_{78}$. It appears to be formed by the action of 7 atoms ammonia on 6 atoms of the acid ether, thus:

$$\underbrace{6\,C_{18} H_8 O_{14}}_{\text{Ethylomeconic acid.}} + 7\,NH_3 + 6\,HO = \underbrace{C_{84} H_{39} N_7 O_{78}}_{\text{Meconamidic acid.}} + 6\underbrace{C_4 H_6 O_2}_{\text{Alcohol.}}$$

If we suppose that the acid contains 6 atoms water of crystallization which are not given off at 100° C., its formula will be $C_{84} H_{33} N_7 O_{72}$; which contains the elements of 6 atoms normal amidomeconic acid + 1 atom ammonia.

$$C_{84} H_{33} N_7 O_{72} = 6\,(2HO . NH^2 . C_{14} H O_{10}) + NH_3.$$

The numbers obtained by analysis do not agree very well with this view of its constitution; but that it is really an amidogen-compound resulting from meconic acid, may be inferred from the fact that when

it is heated with a solution of potash, ammonia is evolved in considerable quantity, and the liquid gives with hydrochloric acid a crystalline precipitate consisting of bimeconate of potash, which, upon subsequent treatment, in the same manner, is converted into meconic acid.

The appropriation of the atom of ammonia among the 6 atoms of amidomeconic acid (if indeed this be the constitution of the compound), appears to have much diminished the basicity of the complex atom, or else the yellow salt is not a neutral one. The amidomeconic acid being bibasic, 6 of its atoms should, in forming a neutral salt, take up 12 atoms ammonia; but it appears to contain only 9 atoms, its formula as deduced from analysis being

$$9\,NH_4O\,.\,C_{84}H_{24}N_7O_{63}+3\,Aq.;$$

and the acid itself considered with regard to its amount of basic water as indicated in the salt, is represented thus:

$$9\,HO\,.\,C_{84}H_{24}N_7O_{63}+6\,Aq.$$

The yellow salt when examined by the microscope does not present any appearance of crystalline structure, but appears to consist of round translucent granules, which, when deposited slowly from dilute solutions, look like small yellow vesicles or air-bubbles. It dissolves readily in hot water, exhaling a decided smell of ammonia; it is very sparingly soluble in hot alcohol, insoluble in cold alcohol. It gradually gives off ammonia when heated in the dry state to 100° C.; at a higher temperature it blackens and fuses.

Attempts were made to prepare the other salts of the acid by precipitating metallic solutions with the ammonia-salt; but no definite products were obtained.

Coupled Ether of Meconic Acid.—Mecono-ethylomeconic Acid.—This is the substance already described as occurring in the process of making the ethers of meconic acid when rectified spirit is employed; it is deposited generally after the first product of ethylomeconic acid is filtered off. On redissolving it in hot water two or three times, and cooling the liquid, a white amorphous powder is obtained, the analysis of which agrees pretty nearly with the formula $C_{32}H_{12}O_{28}$, which contains the elements of 1 atom meconic and 1 atom ethylomeconic acid:

$$C_{32}H_{12}O_{28}=3\,HO\,.\,C_{14}HO_{11}+2\,HO\,.\,C_4H_5O\,.\,C_{14}HO_{11}.$$

That the substance is more than an accidental mixture appears from its behaviour with ammonia. On adding alcohol to a concentrated aqueous ammoniacal solution of the substance, a deposit appears consisting of small radiated silky tufts; and when such an aqueous solution is evaporated to dryness at 100° C., a crystalline residue remains, which is very sparingly soluble in boiling water; the more

soluble portion gives with hydrochloric acid a crystalline precipitate in the form of needles. Want of material prevented the further examination of these products.

Biethylomeconic Acid, $HO.2C_4H_5O.C_{14}HO_{11}$.—This substance is found in considerable quantity in the acid mother-liquors from which the bodies before described have been deposited, especially when absolute alcohol has been used, its proportionate amount appearing to depend on that of the hydrochloric acid gas passed through the solution. It remains, on evaporating the liquid till acid ceases to be evolved at 100° C. in the form of a thick oil or viscid mass, which becomes a crystalline solid on cooling. It may be purified by recrystallization.

The same compound may be obtained by distilling meconic acid with absolute alcohol and strong sulphuric acid. Alcohol and ether distil over, and a syrupy mass remains, which, when poured into a comparatively large quantity of cold water, yields after a while a crystalline precipitate of a rose-pink colour. On recrystallization from water, it formed colourless flattened prisms, which, when dried at 100°, were found to be identical in composition with the above. Rectified spirit cannot be substituted for absolute alcohol in this process.

Biethylomeconic acid, in its pure state, as crystallized from water, occurs in the form of long, flattened, colourless prisms; under boiling water it fuses before dissolving. It is very soluble in alcohol. In the dry state it fuses at about 110° C. to a yellowish transparent liquid. Its aqueous solution readily coagulates white of egg, has an acid reaction, and decomposes carbonates with effervescence. It imparts a red colour to ferric salts. It is monobasic.

Biethylomeconate of Ammonia.—When ammoniacal gas is passed through a solution of the ether in nearly absolute alcohol, the whole becomes a yellow nearly solid mass; and this when freed by pressure from the ammoniacal alcohol, and dissolved in hot spirit, crystallizes in tufts of radiated, yellow, silky needles. This salt contains no water, its composition being expressed by the formula,

$$NH_4O.2C_4H_5O.C_{14}HO_{11}.$$

Biethylomeconate of ammonia dissolves readily in cold water, forming a yellow solution from which acids throw down the unchanged ether. The solution gives the following reactions: With nitrate of silver a yellow gelatinous precipitate, insoluble in boiling water, and apparently unaltered by elevation of temperature; with sulphate of copper, a green gelatinous precipitate; with acetate of lead, a heavy yellowish-white; with sulphate of magnesia, a crystalline precipitate; with the chlorides of barium, strontium, and calcium, it produces pale yellow, semi-gelatinous precipitates, inso-

luble in boiling water, but readily soluble in excess of the earthy salts. The baryta-salt dried at 100° C. has the composition

$$BaO . 2 C_4 H_5 O . C_{14} HO_{11}.$$

Biethylomeconic acid, when *heated* with ammonia, appears to undergo a change, the result of which is probably an acid amide.

On some Salts and Decomposition-Products of Pyromeconic Acid.

By James Brown.*

Pyromeconic acid was discovered by Sertürner, and long regarded as sublimed meconic acid, till Robiquet, in 1832, obtained meconic acid, the substance from which pyromeconic acid is formed, and showed that the acid obtained from opium exhibits characters different from those of the sublimed acid. He prepared the lead-salt of pyromeconic acid, and showed that its formula is $PbO. C_{10} H_3 O_5$. Liebig pointed out that pyromeconic acid has the same composition as pyromucic acid, and regarded it as probable that the two acids were identical. This supposition, however, has been completely refuted by Stenhouse.

The pyromeconic acid used in the following investigation was prepared by distilling impure meconic acid (prepared by twice treating crude meconate of lime with hydrochloric acid) at a temperature between 260° and 315° C. It was purified by once pressing it between bibulous paper, and then subliming at rather a low temperature, in a cylindrical vessel fitted with a number of transverse diaphragms of filtering-paper. By this treatment, the acid was obtained colourless and pure enough for the preparation of all its salts and products of decomposition.

The acid thus obtained assumes the form of large, beautiful, transparent tables, which dissolve readily in water and alcohol, both at high and at low temperatures, from which solutions it again crystallizes in tolerably large four-sided prisms. It is slightly acid to litmus-paper, and retains this acid reaction even after three crystallizations from boiling water. It volatilizes completely at 100° C., a property which may be used to test its purity from parameconic acid (with which it is always contaminated at the first sublimation), inasmuch as the latter requires a much higher temperature to volatalize it.

Pyromeconic acid gives a deep red colour with ferric salts, and forms no precipitate with the chlorides of calcium, barium and man-

* Phil. Mag. [4], IV, 16.; Ann. Ch. Pharm. LXXXIV, 32.

ganese, or with sulphate of magnesia, either at high or at low temperatures, even on the addition of ammonia. With corrosive sublimate, it forms after a while a white amorphous precipitate which redissolves on boiling. On treating a hot aqueous solution of pyromeconic acid with strong caustic potash in excess, and leaving it to stand for some hours, it soon yields crystals consisting of the acid in its original state. A similar experiment was made with ammonia, but it led to the same result: in both cases, the liquid became nearly black.

The formula of pyromeconic acid is $HO . C_{10} H_3 O_5$. or $C_{10} H_4 O_6$.

Pyromeconate of Baryta.—Obtained by mixing a warm ammoniacal solution of pyromeconic acid with acetate of baryta, the salt being then deposited, after a short time, in small, colourless, silky needles. In dilute solutions they do not form immediately, but their formation goes on very quickly when once begun.

This baryta-salt is the most soluble of all the earthy pyromeconates: water at 15·5° C. dissolves 2·50 per cent of it. It is but slightly soluble in alcohol. Like all the pyromeconates, it has a strong alkaline reaction, and gives with sesquichloride of iron a faint red colouring, which, however, is stronger when crystals of the salt are used instead of the solution. On evaporation *in vacuo*, the salt is deposited in short prisms of a yellowish colour. It loses nothing in weight by exposure to a temperature of 100°, but when more strongly heated, it burns with slight incandescence, without previously melting. The salt, when thoroughly washed with alcohol and dried at 100° C., was found to contain $BaO . C_{10} H_4 O_6$, or $BaO . C_{10} H_3 O_5 + HO$.

Pyromeconate of Strontia, $SrO . C_{10} H_3 O_5 + HO$.—On mixing an alcoholic solution of nitrate of strontia with an alcoholic solution of pyromeconic acid which has been made ammoniacal, a precipitate is immediately formed, consisting of small, silky needles, which, by recrystallization from water may be obtained in stellate groups having a yellowish colour. The salt obtained by precipitation is colourless, slightly soluble in water and alcohol at ordinary temperatures, more soluble at higher temperatures, and has a strong alkaline reaction. Water at 20° C. dissolves 1·3 per cent of it. It does not lose weight at 100°; at higher temperatures it does not melt, but burns with a slight explosion.

Pyromeconate of Lime, $CaO . C_{10} H_3 O_5 + HO$.—Obtained in the form of small, colourless, silky needles by adding an excess of a solution of acetate of lime to a warm ammoniacal solution of pyromeconic acid. It is slightly soluble in warm alcohol, somewhat more soluble in water, from which it crystallizes as the solution gradually cools, in crystals of considerable magnitude. Water at 15·5° C. dissolves 0·31 per cent of it.

Pyromeconate of Magnesia, $MgO . C_{10} H_3 O_5$.—A warm aqueous solution of pyromeconic acid forms with acetate of magnesia a white

amorphous precipitate insoluble in water and alcohol. The reactions of this salt are exactly like those of the other pyromeconates. It does not lose weight at 100°. It appears to be the only earthy pyromeconate which contains no water.

Pyromeconate of Lead, $PbO.C_{10}H_3O_5$.—Robiquet obtained this salt by adding hydrated oxide of lead to a hot solution of pyromeconic acid. It may also be formed by adding a warm concentrated ammoniacal solution of pyromeconic acid to acetate of lead, whereupon there is immediately deposited a dense crystalline powder, which rapidly increases if the liquid be briskly stirred. The crystals are but sparingly soluble in hot water, and still less soluble in alcohol whether hot or cold. The precipitated salt is colourless, but when exposed to daylight quickly turns yellow. It does not lose weight at 100°, even in the course of three or four hours.

Pyromeconate of Copper, $CuO.C_{10}H_3O_5$.—Stenhouse obtained this salt by boiling the acid with hydrated oxide of copper, and leaving the filtered solution to cool. It may also be formed by mixing ammonis-sulphate of copper with a warm aqueous solution of pyromeconic acid; a precipitate is then formed, consisting of green, shining, crystalline needles, which are very brittle and easy to pulverize. The crystals require a tolerably large quantity of hot water to dissolve them; in cold water and in alcohol they are but very slightly soluble.

Pyromeconate of Ferric Oxide, $Fe_2O_3\,3.C_{10}H_3O_5$.—This salt has been fully described by Stenhouse, who obtained it by boiling pyromeconic acid with hydrated ferric oxide, or with ferric sulphate. It may likewise be formed by adding sesquichloride of iron to a hot concentrated aqueous solution of the acid; cinnabar-coloured crystals then gradually appear, and attach themselves to the sides and bottom of the vessel.

DECOMPOSITION-PRODUCTS OF PYROMECONIC ACID.

When a few crystals of pyromeconic acid are moistened with strong nitric acid, they immediately assume a white gelatinous appearance, and bubbles of nitrous acid are soon given off. On applying a moderate heat, the action becomes extremely violent, and remains so, even if the application of heat be discontinued; oxalic acid and hydrocyanic acid are simultaneously produced.—Sulphuric acid does not act on pyromeconic acid in the cold, but dissolves it at a gentle heat, forming a colourless liquid, from which the pyromeconic acid is again deposited on cooling.—When chlorine is passed into a solution of pyromeconic acid, no substitution-product is formed, the action being apparently too violent for that result; in fact, the acid is completely decomposed, and the liquid is afterwards found to contain oxalic acid, though not in large quantity.—The author did not succeed in form-

ing an ether by passing dry hydrochloric acid gas through a solution of the acid in absolute alcohol, the crystals which separated out from the liquid proving to be nothing but the unaltered acid.

Action of Bromine on Pyromeconic Acid.—When bromine water is added to a strong aqueous solution of pyromeconic acid, the latter being in excess, the bromine is quickly taken up, and there remains a colourless liquid, which, after standing for an hour or less, deposits beautiful, small, colourless crystals of *Bromopyromeconic Acid*, $C_{10}\left\{\begin{matrix}H_3\\Br\end{matrix}\right\}O_6$. This acid is slightly soluble in cold water, somewhat more soluble in hot water, and reddens litmus slightly. It dissolves readily in boiling alcohol, and crystallizes from this solution in beautiful tables, which, however, if the cooling be carefully conducted, are replaced by short prisms. With ferric salts, the acid gives a deep purple-red colour, totally distinct from the red produced by the original acid. Nitric acid decomposes it with effervescence, but sulphuric acid dissolves it without visible decomposition. When subjected to dry distillation, it fuses and afterwards blackens, giving off hydrobromic acid in large quantity. If the heat be allowed to act upon it for a longer time, a white crystalline substance begins to collect in the cold part of the tube; but the quantity of this substance obtained was too small for examination. The acid gives no precipitate with nitrate of silver, and does not reduce the oxide to metallic silver on boiling; neither does it produce any precipitate in solutions of chloride of barium, chloride of calcium, or sulphate of magnesia, even in presence of ammonia. With ammonio-sulphate of copper it exhibits no reaction in the cold, but on the application of heat a bluish precipitate is formed.

Bromopyromeconic acid is monobasic, like pyromeconic acid.

Lead-salt, $PbO.\ C_{10}\ H_3\ Br\ O_5 + HO$.—A warm alcoholic solution of the acid forms, with an alkaline solution of acetate of lead, a white precipitate, consisting of small, dense, crystalline needles, which quickly settle down to the bottom of the vessel. This salt may also be obtained by mixing the aqueous solutions of the acid and of acetate of lead, and adding ammonia; but when thus prepared, it is very dark-coloured. It does not lose weight at 100°.

The author has likewise obtained a substitution product of pyromeconic acid with iodine.

Researches on Chemical Affinity.

By R. Bunsen.*

FIRST MEMOIR.

The force which is regarded as the cause of chemical affinity may, as is well known, be increased and diminished by various influences. Its magnitude varies under the influence of light, heat, and electricity; it changes with the proportion of the acting masses, and is essentially modified by the state of aggregation of matter, as well as by the contact of the acting body with bodies substantially different. It may, therefore, be regarded as a function of all these influences. If the mathematical form of this function could be determined, it would afford a measure of the absolute magnitude of the force itself.

Claude Berthollet, the celebrated author of the "Statique Chimique," was the first to regard the cause of chemical phenomena from this point of view. His sagacious contemplations led him to assume that particular law of the action of masses, which was named after him, and is still at the present day regarded as valid, and by which he thought he could express the relation of the force of chemical affinity to the mass of the combining bodies. According to this law, a body, to which two different substances capable of uniting chemically with it, are presented in different proportions, divides itself between these substances, in the ratio of the products of their relative masses into the absolute strengths of their chemical affinities for it. Thus, if the masses of the two bodies which are present in excess be denoted by A and B, the respective coefficients which denote their absolute affinities for the body C by α and β, and the quantities of A and B which actually combine with C by a and b; then will these quantities be to another as αA, βB, i. e.:

$$a : b = \alpha A : \beta B.$$

Hence the rates of the absolute affinity of A to C, and B to C, is given by the equation:

$$\frac{\alpha}{\beta} = \frac{aB}{bA}$$

It appeared to me a matter of great interest to subject this law, which as yet is destitute of any experimental support, to an exact investigation. The result of this examination has been to establish not Berthollet's, but a totally different law, which promises to exert a not unimportant influence on our views of the mode of action

* Ann. Ch. Pharm. LXXXV, 137.

of chemical affinity. The substance of this new law may be comprised in the following theorems.

1. When two or more bodies, B, B', are presented in excess to the body A, under circumstances favourable to their combination with it, the body A always selects of the bodies $B, B' \ldots$. quantities which stand to one another in a simple stoïchiometrical relation; so that for $1, 2, 3 \ldots$. atoms of the one compound, there are always formed $1, 2, 3, 4 \ldots$. atoms of the other.

2. If in this manner there is formed an atom of the compound $A' + B'$ in conjunction with an atom of $A + B$, the mass of the body B may be increased relatively to that of B' up to a certain limit, without producing any change in that atomic proportion.

3. When a body A exerts a reducing action on a compound $B + C$, present in excess, so that A and B combine together, and C is set free; then if C can, in its turn, exert a reducing action on the newly formed compound, the final result of the reaction is such, that the reduced part of $B + C$ is to the unreduced portion in a simple atomic proportion.

4. In these reductions, also, the mass of the one constituent may, without altering the existing atomic relation, be increased up to a certain limit, above which that relation undergoes changes by definite steps, but always in the proportion of simple rational numbers.

It is not surprising that these remarkable relations have hitherto passed unobserved, seeing that they only arise when the phenomena of combination, which are regulated by them, take place quite simultaneously. For even if the body A were originally to select for combination from the bodies B and C, quantities bearing to one another a simple atomic relation, but the combination of A and B were to take place in shorter time than that of A and C, it would follow of necessity that, during the whole term of the process, the ratio of B to C, and consequently also the mutual atomic relation of the associated compounds would change, so that the observed proportion would be no longer definite, but mixed. The same result must follow, if the bodies which are combining side by side be not homogeneously mixed in the beginning. The law will, therefore, be most easily recognisable when these relations do not exert a disturbing action, as, for example, in combustible gases, which before combustion exist in a condition of static equilibrium. I shall, therefore, in the following investigations, chiefly avail myself of such mixtures.

When carbonic oxide and hydrogen are exploded with a quantity of oxygen not sufficient to burn them completely, the oxygen divides itself between the two gases, according to the law above mentioned, in such a manner that the quantities of carbonic acid and water produced, stand to one another in a simple atomic proportion.

The combustions were made in a eudiometer, which allowed the

pressure to be varied at pleasure. (For the description of the apparatus, see the original Memoir). The hydrogen used in the experiments was obtained by electrolysis, and the carbonic oxide by the action of sulphuric acid upon formiate of magnesia; the latter, after being washed with potash-ley, was found to be quite pure.

I. A mixture of detonating gas (2 vol. H + 1 vol. O, obtained by electrolysis), and carbonic oxide, containing, in 100 parts:

Carbonic oxide	72·57
Hydrogen	18·29
Oxygen	9·14
	100·00

was divided into two portions. The first portion, burnt in the dark at $0^{m}{\cdot}7338$ and 22·3° C., gave for the proportions of CO and H consumed:

	Found.		Calculated.
Carbonic oxide . . .	12·28	2 vols.	12·19
Hydrogen	6·00	1 vol.	6·09
	18·28		18·28

II. The second portion, burnt in the dark at $0^{m}{\cdot}7324$ and 22·5° C., gave:

	Found.		Calculated.
Carbonic oxide . . .	12·09	2 vols.	12·19
Hydrogen	6·19	1 vol.	6·09
	18·28		18·28

III. A similar mixture, containing, in 100 parts:

Carbonic oxide	59·93
Hydrogen	26·71
Oxygen	13·36
	100·00

when burned in daylight, at $0^{m}{\cdot}3952$ and 22·5° C., gave, for the quantities consumed, in 100 parts:

Carbonic oxide . . .	13·06	1 vol.	13·36
Hydrogen	13·66	1 „	13·36

In Exp. I. and II., the ratio of the oxygen to the combustible gases was 10 : 99·4, and that of the hydrogen to the carbonic acid, 10 : 39·7. The mixture gave, in two combustions, the proportions of 1 vol. hydrogen burned to 2 vols. carbonic oxide.

In Exp. III., a gaseous mixture, containing only 64·9 vols. combustible gases to 10 vols. oxygen, and only 22·2 vols. carbonic oxide to 10 vols. hydrogen, gave equal volumes of the gases consumed.

In the following experiments, a mixture was used containing:

Carbonic oxide	36·70
Hydrogen	42·17
Oxygen	21·13
	100·00

IV. The gas was burned in three portions; the first, burned in sunshine at $0^{m}{\cdot}7264$ and 22·5° C., gave for the quantities consumed:

	Found.		Calculated.
Carbonic oxide . . .	11·01	1 vol.	10·56
Hydrogen	31·25	3 vols.	31·70
	42·26		42·26

V. The second portion, burned in the dark at $0^{m}{\cdot}7230$ and 22·6° C., gave:

	Found.		Calculated.
Carbonic oxide . . .	10·65	1 vol.	10·57
Hydrogen	31·61	3 vols.	31·69
	42·26		42·26

VI. The third portion, burnt in daylight at $0^{m}{\cdot}3169$ and 22° C., gave:

Carbonic oxide . . .	10·71	1 vol.	10·59
Hydrogen	31·55	3 vols.	31·67
	42·26		42·26

VII. The next experiment was made with a mixture containing in 100 vols.:

Carbonic oxide	40·12
Hydrogen	47·15
Oxygen	12·73
	100·00

Burned in daylight at 23° C. and $0^{m}{\cdot}7200$, it gave for the quantities consumed:

	Found.		Calculated.
Carbonic oxide . . .	4·97	1 vol.	5·09
Hydrogen	20·49	4 vols.	20·37
	25·46		25·46

VIII. Another mixture, of unknown composition, gave:

	Found.		Calculated.
Carbonic oxide . . .	4·95	1 vol.	5·07
Hydrogen	10·27	2 vols.	10·15

In the mixture with which the Experiments IV., V. and VI. were made, the oxygen was to the combustible gases as 10 : 37·3, and the hydrogen to the carbonic oxide as 10 : 8·7. The three experiments show that the volumes of H and CO consumed were as 3 : 1, whether the pressure to which the gases were subjected was $0^{m}{\cdot}7264$, or $0^{m}{\cdot}3169$, and whether the combustion took place in the dark, or in daylight. In Exp. VII., the oxygen was to the combustible gases as 10 : 68·5, and the hydrogen to the carbonic oxide as 10 : 8·5. From this mixture, the oxygen took 4 vols. H to 1 vol. CO. Lastly, in Exp. VIII., the combustion produced 2 vols. vapour of water to 1 vol. carbonic acid.

The proportions of hydrogen and carbonic oxide consumed on these several gaseous mixtures, correspond to five hydrates of carbonic acid of the following forms:

$$HO.\,2\,CO_2;\ HO.\,CO_2;\ 2\,HO.\,CO_2;\ 3\,HO.\,CO_2;\ 4\,HO.\,CO_2.$$

Hence it might be imagined, that the cause of the combustion taking place in these atomic proportions is to be found in the actual formation of these hydrates. Closer consideration, however, will show that such a supposition is wholly untenable. It may, indeed, be easily shown that carbonic acid does not form any definite compound with water—at least, at ordinary temperatures. The author has shown (in a research not yet published, on the absorption of gases by liquids), that the coefficient of absorption of carbonic acid by water, which is 0·8545 at 19·6° C., and 1·4698 at 4·4° C., varies exactly in proportion to the density of the gas, at least, within the limits observed, and consequently exhibits a relation which is totally inconsistent with the formation of a hydrate of carbonic acid. Hence it is impossible to believe that carbonic acid can form as many as four or five definite compounds with water. But even if this supposition were admissible, it would still be contrary to all chemical experience that the compound $2\,HO.\,CO_2$ should be formed at the lowest, the compound $3\,HO.\,CO_2$ at a higher, and the hydrate $4\,HO.\,CO_2$ at the highest temperature. We find, on the contrary, in all cases hitherto observed, that the lower hydrates of acids bear, without decomposition, much higher temperatures than those which contain a larger quantity of water. We cannot, therefore, suppose that the compound $4\,HO.\,CO_2$, formed at the highest temperature, is incapable of existing at a lower temperature, and that instead of it only the compounds $3\,HO.\,CO_2$, $2\,HO.\,CO_2$, or $HO.\,CO_2$, are formed. But there is yet another circumstance which speaks most decidedly against this hypothesis. All the known compounds of acids with several

atoms of water are incapable of existing at very high temperatures, whereas, these hydrates of carbonic acid, if they exist, must be formed only at the highest temperatures, and must, on cooling, be again resolved into carbonic acid and water. And even if all these contradictions could be reconciled, by the assumption that at the high temperatures at which the combustion of the gases takes place, the combining tendencies may be the reverse of those which are observed at lower degrees of heat, we should still only encumber ourselves with new difficulties; for there are other phenomena relating to the same point, which even this assumption is unable to explain.

When oxygen is passed over red-hot charcoal, carbonic acid is formed; but this gas, by the further action of the charcoal, is completely converted into carbonic oxide. If the oxygen gas be replaced by vapour of water, the charcoal is likewise oxidized, and hydrogen separated. The action does not, however, proceed to the complete formation of carbonic acid, but stops when for every 4 vols. hydrogen separated, there have been formed exactly 1 vol. carbonic acid, and 2 vols. carbonic oxide. A gaseous mixture, obtained by this process, gave by analysis the following results:

	Found.		Calculated.
Hydrogen	56·52	4 vols.	57·14
Carbonic oxide . . .	28·71	2 „	28·57
Carbonic acid	14·77	1 vol.	14·29
	100·00		100·00

The same composition is found in a similar gaseous mixture analysed more than fifty years ago by Clement and Desormes:

Hydrogen	56·22
Carbonic oxide	28·96
Carbonic acid	14·63
Marsh-gas	0·19
	100·00

If, now, we suppose that the simple atomic relation of the simultaneously formed products of decomposition results from a combination formed according to the same proportion, we are met by an irreconcilable contradiction. For since the products of oxidation thus formed contain 4 atoms oxygen to 3 atoms carbon, we should, on the hypothesis just mentioned, be obliged to admit that a body having the composition of mesoxalic acid is formed at a red heat, and resolved on cooling into carbonic oxide and carbonic acid,—unless indeed we were to take refuge in the still more absurd supposition that an organic compound, $C_3H_4O_4$, corresponding in composition to the decomposition-products obtained, has actually existed at the red heat, but has been resolved on cooling into hydrogen, carbonic oxide and carbonic acid.

Especially remarkable is the behaviour of cyanogen when imperfectly burned. Nitrogen is then set free, and carbonic acid and carbonic oxide produced in quantities which bear to one another, as the law requires, a simple atomic relation. The experiment is difficult, inasmuch as the combustion must be made at a temperature low enough to prevent any partial oxidation of the nitrogen. To this end it is necessary to ascertain by preliminary experiments the limits of inflammability of cyanogen, and then, having made a mixture in proportions near that limit, to compress it so far that the limit of inflammability may be just passed, and the combustion in the eudiometer may take place without sublimation of mercury. In this manner a mixture of cyanogen, free oxygen and atmospheric air containing in 100 parts:

Cyanogen	18·05
Oxygen	28·87
Nitrogen	53·08
	100·00

yielded by combustion the following products:

Nitrogen	17·42	3 vols.	17·42
Carbonic oxide . . .	11·93	2 vols.	11·61
Carbonic acid . . .	22·90	4 vols.	23·22
	52·25		52·25

Hence it appears that the oxygen unites with the carbon of the cyanogen, not to form carbonic acid or carbonic oxide alone, but both together, and moreover in a simple atomic proportion, as if the compound $CO \cdot 2\,CO_2$ or C_3O_5 had been formed. As it is not possible by altering the proportions of this mixture to attain the limit at which this particular proportion passes into another, without incurring the disturbing effect of a simultaneous oxidation of the nitrogen, I have been obliged to give up the further prosecution of the experiments with mixtures containing cyanogen.

A wider range is afforded by experiments with a mixture of carbonic acid with hydrogen and oxygen, in the combustion of which the carbonic acid is exposed at the same time to the reducing action of the hydrogen and the oxidizing action of the oxygen. These experiments demonstrate the remarkable fact that the phenomena of reduction likewise take place in such a manner that the reduced and unreduced portions of the compound bear to each other a simple atomic relation.

The contraction which a mixture of carbonic acid and hydrogen suffers by combustion with detonating gas is equal to the volume of the carbonic oxide formed. Moreover, as the latter is equal to that of the carbonic acid reduced, we have only to deduct the observed contraction from the volume of carbonic acid originally present in the

mixture, and the difference will give the portion of carbonic acid which has escaped reduction.

A mixture of carbonic acid, hydrogen and detonating gas containing 8·52 per cent carbonic acid, 70·33 hydrogen and 21·15 oxygen, yielded in this manner 3 vols. carbonic oxide to 2 vols. carbonic acid, just as if 5 atoms CO_2 had been reduced to the compound $C_5 O_7$, or as if the compound $3\,CO.\,2\,CO_2$ had been formed.

The gas remaining after the combustion in the last experiment was again mixed with detonating gas in such proportion as to form a mixture containing 4·41 per cent carbonic oxide, 2·96 carbonic acid, 68·37 hydrogen and 24·26 oxygen. The combustion produced an expansion, showing that a portion of carbonic oxide had been burnt and converted into carbonic acid; and the quantity of CO thus oxidized was to that which remained unaltered as 1 vol. to 3 vols. corresponding to the compound $C_4 O_5$ or $3\,CO, CO_2$.

On collecting the results of all these experiments, it appears that the reducing and oxidizing actions of oxygen are exerted as if the following compounds were thereby produced:

$$2\,CO.\,CO_2;\ 3\,CO.\,CO_2;\ 3\,CO.\,2\,CO_2;\ HO.\,2\,CO_2;\ HO.\,CO_2;$$
$$2\,HO.\,CO_2;\ 3\,HO.\,2\,CO_2;\ 4\,HO.\,2\,CO_2.$$

If the formulæ thus determined, nearly all of which correspond to unknown compounds, could be regarded as the expressions of really existing substances, a mode would be found of determining beforehand, by experiment, the atomic relations of compounds yet unknown. But whatever signification may be attached to these remarkable formulæ, and whatever other relations may lie hid in them, they must even now be regarded as the expression of a peculiar mode of action of chemical affinity; and the numbers which enter into them must be distinguished, as *coefficients of affinity*, from the atomic numbers which are *coefficients of combination*.

Although the results of the preceding investigation must modify considerably our ideas of the mode of action of chemical affinity, I refrain for the present from any interpretation of the law above enumerated. It appears to me to be essential to ascertain whether the same law holds good for liquids, and to assign the conditions which determine the alteration of the coefficients of affinity. The limits at which these coefficients suddenly pass from one rational proportion to another, and at which therefore the force of affinity is, as it were, in a state of instable equilibrium, promise to afford the most important revelations respecting the influence of other forces, which are here certainly to be detected in their minutest workings, namely, of light and heat, and likewise of mass and contact. These relations will form the subject of a future Memoir.

On the Constitution of Iodide of Nitrogen.

By R. Bunsen.*

That the elements of water are not concerned in the formation of iodide of nitrogen, follows from the simple fact that a concentrated solution of iodine in absolute alcohol, on being saturated with anhydrous ammonia, yields iodide of nitrogen without any decomposition of the solvent. Hence we may conclude that iodide of nitrogen contains no oxygen, but only nitrogen, iodine and hydrogen. Moreover, since in the formation of this compound from iodine and ammonia, there is but one secondary product obtained, viz. hydriodic acid, it follows that the so-called iodide of nitrogen must be a substitution-product of ammonia, in which the hydrogen is wholly or partially replaced by ammonia, viz.:

1. $NH_3 + 6\,I + x\,I = N\,I_3 + 3\,HI + x\,I$
2. $NH_3 + 4\,I = NH\,I_2 + 2\,HI$
3. $NH_3 + 2\,I = NH_2I + HI$

Either of the compounds, 1, 2 or 3, might however contain ammonia or hydriodic acid in addition. But it is easily shown that hydriodic acid cannot enter into the composition of iodide of nitrogen; for this substance dissolves in hydrochloric acid without evolution of gas, forming a liquid which contains ammonia and *protochloride of iodine*, but no hydriodic acid. This reaction shows indeed that iodide of nitrogen is a compound of the form NI_3, NHI_2 or NH_2I, either alone or combined with the elements of ammonia. Which of these two alternatives is the correct one may be easily decided, if we can find the atomic proportion which the products of the decomposition of iodide of nitrogen by hydrochloric acid bear to each other. For if *ammonia* and *protochloride of iodine* are the only products thus formed, the decomposition must take place in one of the following ways:

4. $N\,I_3 + 3\,HCl = 3\,ICl + NH_3$
5. $NH\,I_2 + 2\,HCl = 2\,ICl + NH_3$
6. $NH_2I + HCl = ICl + NH_3$

Hence it appears that the so-called iodide of nitrogen must be, so to speak, a nitrile, an imide, or an amide of iodine, according as 3, 2 or 1 atom of protochloride of iodine is separated for each atom of ammonia. Similarly we may infer that the separation of 2 atoms of ammonia to 3 atoms of protochloride of iodine would correspond to

* Ann. Ch. Pharm. LXXXIV, 1.

the compound NH_3+NI_3, and the separation of 2 atoms of ammonia to 1 atom of protochloride of iodine to the compound NH_3+NH_2I. It follows that the composition of iodide of nitrogen may be determined by the products of its decomposition by hydrochloric acid, viz.:

I. By the quantity of ammonia formed.
II. By the composition and quantity of the chloride of iodine.

The ammonia is determined as usual by precipitation with chloride of platinum.—To determine the chloride of iodine the following method was used:

Two equal volumes of the hydrochloric solution of iodide of nitrogen are taken. In the one, the iodine is precipitated by chloride of palladium, after the chloride of iodine has been converted by sulphurous acid into hydrochloric and hydriodic acid. Let the quantity of iodine thus found be i. A known volume of an aqueous solution of sulphurous acid is then taken, in which the quantity of iodine $i_{,}$ required to decompose the sulphurous acid has been determined by a preliminary iodometric experiment. To this solution the second portion of the hydrochloric acid solution of the iodide of nitrogen is added, and the quantity of iodine $i_{,,}$ then required to decompose the sulphurous acid then determined by similar means. The quantity of chlorine c contained in the chloride of iodine is then given by the equation:

$$\frac{Cl}{I}(i_{,}-i_{,,}-i)=c.$$

Lastly, another equal volume of the hydrochloric acid solution is evaporated over the water-bath till all the chloride of iodine is driven off, and the ammonia is determined by precipitation with chloride of platinum.

The iodide of nitrogen used for the analysis was prepared by mixing cold saturated solutions of iodine and ammonia in absolute alcohol. A black powder was precipitated, which could be washed with absolute alcohol without suffering the slightest decomposition. The product thus obtained was dissolved while yet moist in dilute hydrochloric acid: it dissolved readily and without evolution of gas. From the resulting solution three equal volumes were measured out. The first gave 0·3290 grm. chloroplatinate of ammonium. The second gave 0·1156 grm. palladium by ignition of the precipitated iodide of palladium. The third was added to a quantity of sulphurous acid which, according to a preliminary experiment, required 241·6 cub. cent. of iodine-solution (containing 0·005 grm. in a cub. cent.) to decompose it, and the quantity of iodine still required for that purpose after the addition of the hydrochloric acid solution, was found to be 131·4 cub. cent.

Hence the quantity of ammonia $=0·02508$; also $i=0·27551$;

$i_{'}=1{\cdot}2080$; $i_{''}=0{\cdot}6570$; whence we find for the products of the decomposition:

	Experiment.	Atomic proportion.
Ammonia . . .	0·02508	2·04
Iodine	0·27551	3·00
Chlorine	0·07701	3·00

that is to say, 2 atoms ammonia to 3 atoms protochloride of iodine. Consequently iodide of nitrogen can be nothing else than a compound of ammonia in which the *whole* of the hydrogen is replaced by iodine, with an atom of undecomposed ammonia, as expressed by the formula NH_3, NI_3: this will appear more plainly from the following comparison of the analytical and calculated results:

Protochloride of Iodine.				Iodide of Nitrogen.			
	Atoms.	Calc.	Found.		Atoms.	Calc.	Found.
Cl	1	21·85	21·85	N	1	3·40	3·46
I	1	78·15	78·15	I	3	92·46	92·33
				NH_3	1	4·14	4·21
ClI		100·00	100·00	$NH_3.NI_3$		100·00	100·00

Results nearly of equal accordance were obtained from the analysis of an iodide of nitrogen prepared by the use of less concentrated alcoholic solutions of iodine and ammonia.

To determine whether iodide of nitrogen precipitated from aqueous solutions has the same composition as that obtained with alcoholic solutions, a dilute solution of iodine in aqua-regia was mixed with ammonia, and the resulting precipitate washed as quickly as possible with such a quantity of cold water, that the remaining mother-liquor could not contain more than 0·01 milligrm. ammonia. The analysis of the washed precipitate, conducted as before, led to the formula $NH_3.4NI_3$:

Protochloride of Iodine.				Iodide of Nitrogen.			
	Atoms.	Calc.	Found.		Atoms.	Calc.	Found.
Cl	1	21·85	21·94	N	4	3·51	3·54
I	1	78·15	78·06	I	12	95·43	95·31
				NH_3	1	1·06	1·15
ClI		100·00	100·00	$NH_3.4NI_3$		100·00	100·00

The great facility with which the ammonio-iodide of nitrogen decomposes, with separation of iodine and nitrogen, when continuously washed with water, renders it difficult to decide directly whether the quantity of ammonia actually found in it is really chemically combined or merely mechanically mixed. But an examination of the de-

composition-products obtained from ammonio-iodide of nitrogen by the action of water, leads inevitably to the conclusion that the ammonia is really chemically combined. To establish this conclusion, it is merely necessary to continue the washing till the greater part of the compound is decomposed, with separation of iodine and nitrogen, then dissolve the remaining impure iodized compound in hydrochloric acid, and examine the solution as before.

If by continued washing, the compound NI_3, free from ammonia, were at last produced, together with free iodine separated as a product of decomposition, the hydrochloric acid solution could not contain more than 1 atom ammonia to 3 atoms chloride of iodine; but if the iodide of nitrogen can only exist in combination with ammonia, then, however long the washing may have been continued, the hydrochloric acid solution will always contain more than 1 atom ammonia to 3 atoms ICl; thus, in the former case:

$$x\mathrm{I} + \mathrm{NI_3} + 3\,\mathrm{HCl} = x\mathrm{I} + 3\,\mathrm{ICl} + \mathrm{NH_3}$$

and in the latter:

$$x\mathrm{I} + \mathrm{NI_3} + x\mathrm{NH_3} + 3\,\mathrm{HCl} = x\mathrm{I} + 3\,\mathrm{ICl} + \mathrm{NH_3} + x\mathrm{NH_3}.$$

To decide the question, therefore, a portion of the iodide of nitrogen used for the analysis was washed for several hours longer with distilled water, and then left to stand for a while suspended in water. On the addition of hydrochloric acid, a considerably quantity of free iodine remained undissolved, The solution, which, besides ammonia and protochloride of iodine, must likewise have contained free iodine, gave, when analysed as above, results corresponding to 1 atom ammonia and 3 atoms protochloride of iodine, together with free iodine.

We may conclude then that the ammonia forms an essential constituent of the so-called iodide of nitrogen, and that besides the compound $NH_3 . NI_3$, there probably exists another, having the composition $NH_3 . 4\,NI_3$. The manner in which these compounds are formed directly from iodine and ammonia, is easily seen from the following equations:

$$2\,\mathrm{NH_3} + 6\,\mathrm{I} = \mathrm{NH_3, NI_3} + 3\,\mathrm{HI}$$

and:

$$4\,(\mathrm{NH_3 . NI_3}) + 3\,\mathrm{HO} = \mathrm{NH_3, 4\,NI_3} + 3\,\mathrm{NH_4O}.$$

On the other hand, their formation from the chloride of iodine obtained by the action of iodine in aqua-regia would be in direct contradiction to the formula NH_3, NI_3, if that chloride were really ICl_3, as sometimes supposed, and not ICl. For the action of ICl_3 on ammonia could not produce NI_3, but only NI. This discrepancy led the author to suspect that the chloride of iodine obtained in the manner just mentioned, is not really a terchloride but a protochloride,—

a supposition which has been fully confirmed by experiments made in the author's laboratory by Mr. Cohn.

The formation of ammonio-iodide of nitrogen by the action of ammonia on chloride of iodine may therefore be expressed by the following equation:

$$2\,NH_3 + 3\,ICl = NH_3 . NI_3 + 3\,HCl.$$

The view here given of this compound likewise gives an easy account of the changes which take place when it explodes. The first products of the explosive decomposition are nitrogen and hydriodic acid:

$$NH_3 . NI_3 = 3\,HI + 2\,N;$$

but the latter, at the higher temperature which accompanies the decomposition, must be resolved for the greater part into iodine and hydrogen; while another part of the acid must unite with another part of the compound to form iodide of ammonium, and thereby set free quantities of iodine and nitrogen equivalent to this ammonia.

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VIII.—*On the Solid Compound obtained by Distilling Stearic Acid with Lime.*

By Thomas H. Rowney, Ph.D., F.C.S.

(Assistant in the College Laboratory, Glasgow.)

Though the solid compounds obtained by the distillation of margaric and stearic acids with lime, have been examined by Bussy, Redtenbacher and Varrentrap, these chemists do not agree in the formulæ given by them to these bodies. Bussy,* to the product obtained from margaric acid, gave the formula $C_{34}H_{33}O$, and to that obtained from stearic acid $C_{68}H_{67}O$. The first of these compounds he named margarone, and the second stearone. Redtenbacher† also describes two compounds: the first, margarone, he considers to be $C_{33}H_{33}O$, and the second to be margarone combined with a hydrocarbon, and to have the formula $C_{45}H_{45}O$, or $C_{33}H_{33}O + C_{12}H_{12}$. Varrentrap‡ likewise gives the formula $C_{33}H_{33}O$ for margarone.

Some time ago, having prepared some of the solid compound by distilling stearic acid with lime, I made an examination of it in order to ascertain the cause of these different statements; but my results differed considerably from those obtained by Bussy, Redtenbacher

* Ann. Ch. Phys. [2] LIII, 1833.

† Ann. Ch. Pharm. XXXV, XXXVI. ‡ Ibid.

and Varrentrap. A reference to their papers on the subject, however, at once made the cause of these different results apparent.

In the following paper I have endeavoured to explain this, first detailing my own experiments, and then comparing the results obtained with those of the previously mentioned chemists.

To obtain the compound, stearic acid as produced in the stearine manufactory was mixed with half its weight of quicklime in an iron pot; this was put into a deep sand-bath and covered with sand, and the distillation carried on rapidly; the distillate whilst hot was quite liquid, but it very soon began to deposit crystals, and when quite cold an abundant crop of crystals was deposited; these were separated from the oily liquid by filtration.

I found the best method of purifying the substance, was to melt it by gently heating it, and then mix some ether with the liquid obtained; by exposure to cold, crystals were deposited; the oily matter retained by the ether was separated from the crystals by filtration. By repeating this process several times, all the oily matter was removed; then, by crystallizing two or three times from boiling ether, the substance was obtained quite pure.

In this state it forms beautiful white crystalline plates, soluble in boiling alcohol, and very soluble in ether; it fuses at 76° C., but after fusion does not solidify until the temperature falls to 72° C.; the fused substance crystallizes on cooling. When cold it may be reduced to powder by rubbing in a mortar, but it becomes highly electrical by friction, so much so, that it is difficult to collect the powder. When heated in a test-tube with strong sulphuric acid, it is decomposed, sulphurous acid is given off, and a black carbonaceous residue left in the tube. Nitric acid does not act upon it even when boiled with it, but it is decomposed when heated with a mixture of strong sulphuric and nitric acids, a volatile oily acid being formed. This decomposition I was not able to follow out, for want of substance. Other oxidizing agents were tried, but with no satisfactory results.

The following numbers were obtained by analysis, the fused substance being employed, and the combustions made with chromate of lead.

I.	·2033	grm. of	substance gave:*
	·2535	„	water.
II.	·1770	„	substance gave
	·5355	„	carbonic acid.

* The carbon of the first and the hydrogen of the second combustion were lost.

III.	·1720	grm.	substance gave
	·5165	„	carbonic acid, and
	·2115	„	water.
IV.	·2155	„	substance gave
	·6477	„	carbonic acid, and
	·2660	„	water.

These numbers correspond to the following percentages:

	I.	II.	III.	IV.	Mean.
C . .	—	82·51	81·89	81·97	82·12
H . .	13·85	—	13·66	13·72	13·74
O . .	—	—	—	—	4·14
					100·00

The numbers required for margarone, $C_{33}H_{33}O$, are:

C	82·84
H	13·80
O	3·36
	100·00

which do not agree very well with those obtained by analysis. The experimental numbers, however, agree better with the following formulæ, of which I have given the calculated numbers.

$C_{27}H_{27}O$.		$C_{28}H_{28}O$.	
C . . .	82·23	C . . .	82·35
H . . .	13·70	H . . .	13·72
O . . .	4·07	O . . .	3·93
	100·00		100·00

It will be seen that the difference in the quantities of carbon and hydrogen in these formulæ is very small indeed, and consequently, that it is difficult to decide which formula to adopt, merely from the analysis of the substance itself; but by obtaining a substitution-product I was led to adopt the formula $C_{28}H_{28}O$, or $C_{56}H_{56}O_2$.

Bussy tried the action of chlorine upon his substance, but obtained no satisfactory results. With bromine I have met with better success; but iodine, even when fused with it, has no action upon it.

When bromine is added to the fused substance in a small flask, it acts upon it immediately, hydrobromic acid being given off, and a red oily liquid remains at the bottom of the flask; this solidifies into a crystalline mass when agitated under water; the excess of bromine

was separated from it by washing, first with dilute ammoniacal water, and then with cold alcohol. To obtain the substance pure, it was dissolved in cold ether, and by allowing the ethereal solution to evaporate spontaneously, tufts of feathery crystals were deposited; the mother-liquor was poured off, the crystals were again dissolved in ether, and the solution allowed to evaporate. When this process had been repeated three or four times, very brilliant crystals were obtained. Under the microscope, these were found to consist of square plates collected together into feathery tufts; when viewed by means of polarized light they exhibit a brilliant display of colours; the original substance, on the contrary, shows no colours. The fusing-point of the bromine-compound was found to be from 43° C. to 45° C.

For analysis, the substance was dried *in vacuo* over sulphuric acid, and the combustions were made with chromate of lead.

I. ·3077 grms. of substance gave
·6740 „ carbonic acid, and
·2710 „ water.

II. ·2836 „ substance gave
·6235 „ carbonic acid, and
·2490 „ water.

II. ·2758 „ substance, burnt with lime, gave
·1810 „ bromide of silver.

	I.	II.	III.	Mean.
C . .	59·77	59·95	—	59·86
H . .	9·78	9·75	—	9·76
Br . .	—	—	27·93	27·93

On comparing these numbers with the three following formulæ, they will be found to agree best with the formula $C_{28}{}^{H_{27}}_{Br}O$, which is the one I have adopted, though this probably is not the true atomic weight of the compound.

$C_{27}{}^{H_{26}}_{Br}O$		$C_{28}{}^{H_{27}}_{Br}O$		$C_{29}{}^{H_{28}}_{Br}O$	
C . .	59·03	C . .	59·70	C . .	60·33
H . .	9·47	H . .	9·58	H . .	9·70
Br . .	28·56	Br . .	27·85	Br . .	27·18

From these experiments, it will be seen that I have obtained results differing from those of previous experimenters on this subject: this difference is caused by the atomic weight of carbon having been

altered, it being lower now than at the time of the previous investigations, and the formulæ of stearic and margaric acids have also been altered. Bussy considered the formula of margaric acid to be $C_{35}H_{34}O_4$, but this has since been altered to its present formula, $C_{34}H_{34}O_4$. Redtenbacher, from his analyses, gives the formula $C_{68}H_{68}O_7$, for stearic acid; but his numbers, when recalculated from the present equivalent of carbon, agree with the formula $C_{34}H_{34}O_4$, and the numbers he gives for margaric acid do not agree with the present formula.

Bussy, after several experiments, considered the compound he obtained by distilling margaric acid with lime, to be derived from the anhydrous acid by losing 1 equiv. of carbonic acid; hence the formula given by him, $C_{35}H_{33}O_3 - CO_2 = C_{34}H_{33}O$. Redtenbacher and Varrentrap also consider this to be the reaction, though the formula given by them differs from Bussy's, owing to the difference in the formula of the acid; but a comparison of the properties of the substance, and the numbers obtained by analysis, shows that the compounds examined by them were the same, and also that they agree with that examined by myself, as will be seen by the following table of the corrected numbers of Bussy's, Redtenbacher's, and Varrentrap's, along with those obtained by myself, and the theoretical numbers:

	Bussy.	Redtenbacher.	Varrentrap.	T.H.R.	Theory $C_{33}H_{33}O$.
C . .	82·20	82·39	82·00	82·12	82·35
H . .	13·51	13·86	13·78	13·74	13·72
O . .	4·29	3·75	4·22	4·14	3·93

The fusing-point of the substance was found to be—

Bussy.	Redtenbacher.	Varrentrap.	T.H.R.
77° C.	77° C.	76° C.	76° C.

The numbers of the compound obtained by Redtenbacher, by distilling stearic acid with lime, and to which he gave the formula $C_{45}H_{45}O$, when corrected, agree with the formula $C_{33}H_{33}O$: they also agree with other formulæ, the percentage difference in the carbon and the hydrogen being very small in the different formulæ, as previously stated. As he only made one analysis of the compound, and the fusing-point is near that of the first compound, it is doubtful whether it really is the true margarone. The compound obtained from stearic acid by Bussy must also be considered doubtful, as the numbers he obtained do not agree with any probable formula.

The experiments of Bussy, Redtenbacher, and Varrentrap,

together with my own, show that stearic and margaric acids, when distilled with lime, yield the same products of decomposition. The solid compound is also obtained under the following circumstances: By distilling the acids *per se;* secondly, by distilling the lime, baryta, or potassa-salts of these acids; and, thirdly, by distilling the acids with lime or baryta.

It will be seen that the decomposition proceeds further in this case, than when acids, lower in this series, are treated in a similar manner. This is probably owing to the high temperature required to distil the compound over.

As the name stearone or margarone is not applicable to this compound, I have given it the provisional name of *Stearene*, until something more definite is known of its constitution.

Since this examination has been finished, Messrs. Delffs and Overbeck* have described three compounds, obtained by distilling the lime or baryta-salts of myristic, cocinic, and laurostearic acids, and which they have named myristone, cocinone, and laurostearone; but I do not think the formulæ given by them are quite correct, as the numbers given by them will agree with several formulæ, the hydrogen in all the analyses being far too high for the formulæ of those compounds; and it is very probable that the compound described as myristone, $C_{50}H_{50}O_2$, is identical with that described in this paper as stearene, $C_{28}H_{28}O$, or $C_{56}H_{56}O_2$, the fusing-point of both being nearly the same, viz.: 75° C. myristone, 76° C. stearene.

This investigation was made in the laboratory of Dr. T. Anderson, to whom I am much indebted for advice during its prosecution.

IX.—*On deposits of soluble or gelatinous Silica in the lower beds of the Chalk formation.*

By J. Thomas Way, F.C.S.

CONSULTING CHEMIST TO THE ROYAL AGRICULTURAL SOCIETY OF ENGLAND.

The author described the discovery which, in conjunction with Mr. J. M. Paine, of Farnham, he had made of large deposits of silica in the condition in which it is readily soluble in solutions of caustic potash or soda when boiled with these solutions at ordinary temperatures in open vessels.

* Chem. Gaz. Nov. 1, 1852.

The beds containing this silica are geologically situate at the base of the chalk formation between the upper green sand and the gault clay. At Farnham, where the beds have been most examined, they are very fully developed, coming to the surface over a considerable breadth of land, and extending to the distance of several miles. Judging from the dip of the strata, and from such sections as the quarries in the neighbourhood afford, the author believes that the total thickness of the deposit in question cannot be at this spot less than from 80 to 100 feet in thickness. It is not, however, of uniform character throughout, but consists of beds of yellowish, light, soft rock, intercalated with loose and apparently sandy marls.

The attention of the author was first drawn to this subject during the examination of a series of specimens representing the strata of the chalk formation, which were collected for analysis about three years ago. On examining some of the lower deposits of this series, he was struck with the circumstance that, though of a yellowish-white colour, of small density, and having every appearance of being chalk marls (under which name they are indeed generally used in agriculture), they did not, in many cases, exhibit the smallest effervescence when treated with an acid, and contained merely a trace of lime in any form.

The following results were obtained from the analysis of a specimen of this earth.

Soluble in acids	Silica	40·30
	Peroxide of iron	2·26
	Alumina	3·44
	Lime	·61
	Magnesia	·47
	Chloride of sodium	·14
	Potash	·43
Insoluble in acids	Silica	41·23
	Alumina, with a little oxide of iron	11·12
	Traces of lime and magnesia	
		100·00

The silica "soluble in acids" is here the total quantity of silica which is soluble in potash after treatment with boiling muriatic acid in the usual way. The quantity of soluble silica directly dissolved out by potash without previous treatment with an acid, is in this case 28·70 per cent. The author observed that the existence of these beds was not altogether unknown before. Since he had been engaged upon this examination, he had found that similar deposits of

soluble silica had been mentioned by Sauvage, in the Annales des Mines, as occurring in the Département des Ardennes, in France. Sauvage had found as much as 56 per cent of soluble silica in these deposits; and from their description it was plain that they were the same beds, although somewhat differing from the corresponding strata in England.

Within the last two years, as many as 80 or 100 samples have been carefully collected by the author and Mr. Paine from the land of the latter at Farnham, and examined in reference to the proportion of soluble silica they contain. In all cases the quantity of soluble silica has been determined by boiling the dry and powdered earth in moderately strong solution of caustic potash or soda, which dissolves the free silica without, as is well known, affecting that portion which is combined with alumina as clay or the silica that may exist as sand.

The quantity of soluble silica so ascertained has been found to constitute from 5 to 72 per cent of the dry earths. As a rule, the deposits which are geologically nearest the gault clay contain the smallest proportion, which increases in the beds as they rise towards the green sand. The largest proportion that has been observed hitherto has been above stated as 72 per cent. This particular bed is at Farnham of about 10 or 12 feet of thickness, and close to the surface of the land on the hill-side. It is very remarkable when dry, on account of its extreme lightness, by which and by its porosity it is easily recognized. Very many of the beds have been found to contain as much as 60 per cent of free soluble silica, and 20 or 30 tons have been sent to London, affording, when ground up, an average amount of 64 per cent. There is therefore no doubt of the beds in question being available as a source of soluble silica if it should be found desirable so to employ them.

The author mentions that although many of the beds contain no carbonate of lime, there are others in which both soluble silica and carbonate of lime are associated. These beds are generally of a harder and more compact character, and are used locally as building-stones. The "firestone," which is quarried to a considerable extent at Godstone and Reigate, in Surrey, and used in London to form the backs of fire-places, is from the same deposit, and of similar composition. Mr. Way has found the building-stone to contain about 25 per cent of soluble silica with 50 per cent of carbonate of lime and 25 per cent of clay.

With the exception of the building and firestone rock, which are of considerable hardness, the other beds are easily reduced to powder;

indeed, when first dug up in the moist state they readily crumble between the fingers. When examined by the microscope the silica is found to be amorphous.

With the exception of a few casts of foraminæ the deposit is not infusorial.

Mr. Way proposes to employ these beds as a source of silicate of lime for agricultural purposes. He finds that the silica can be made to combine with lime with great ease in several ways: a mixture of slaked lime with the powdered rock, when made into a thin mortar, and left for several weeks, is found to be entirely converted into silicate of lime. The process is hastened by adding 2 or 3 per cent of carbonate of soda, which becoming caustic, dissolves the silica, forming a soluble silicate, which is subsequently decomposed by the lime; and in this way, the soda acting as a carrier between them, causes a speedy union between the silica and lime.

Another method of producing the silicate of lime, is to mix the slaked lime with the powdered rock and sufficient water to bring the mixture to the thickness of gruel, and to heat to nearly the boiling-point; the combination is complete in about an hour. In all cases the silica is used in the proportion of 3 equivs. to 1 equiv. of lime.

A mixture of the rock with chalk, when heated to low redness in a reverberatory furnace, gives the compound in a very fit condition for agricultural use; but it is necessary that the heat should be carefully regulated, otherwise the silicate becomes altogether insoluble in water.

The author has found silicate of lime produced in either of the above ways soluble to the extent of about 20 grains in the gallon of distilled water; and as the largest portion of the 20 grains so dissolved is silica, he considers this solubility sufficient in relation to the quantity of water passing through plants, to supply all the silica required by wheat, barley and other plants of the silicious class.

He proposes to employ the silicate of lime as a manure for light lands, and he anticipates that it will serve to correct the over-luxuriance and tendency to be "laid," which is so common in well-manured light soils, and that it will render the use of guano and other nitrogenous manures more certain and more admissible on such lands.

Mr. Way, in conclusion, suggests a possible connection between the existence of these beds and the production of the chalk itself. He thinks it certain that the deposits of soluble silica can only have been formed from solution and in the absence of heat. Silicate of lime, derived by disintegration from the older rocks, many of which contain it in abundance and dissolved in water, may be supposed to

be acted upon by carbonic acid derived from the decomposition of animal and vegetable matter or from volcanic sources. The results of such an action would be the production both of carbonate of lime and of soluble silica. The author points out as an interesting fact, that we not only find the chalk closely associated with the silica beds, but that in the case of the building and firestone before described, they are in some cases intimately mixed, which could hardly have occurred if the two deposits were not due to some common origin.

X.—*On a Compound Sulphate of Potash and Soda.*

By J. H. Gladstone, Ph.D., F.R.S., F.C.S.

The saturating power of the common organic acids, is a subject to which great attention has been and still is paid. Many acids that were once considered monobasic have had their equivalents doubled or trebled, with evident advantage in the explanation of their salts. To take one example: Tartaric acid, formerly viewed as $HO, C_4H_2O_5$, is now represented as $2\,HO, C_8H_4O_{10}$, and its bibasic character explains at once why, if half the quantity of potash necessary for its saturation be added to a solution of the acid, we obtain not a mixture of neutral salt and free acid, but a sparingly soluble bitartrate; and why we have such an endless variety of double tartrates, even one, Rochelle salt, in which the two alkalies, potash and soda, are united, although they are bases of the same natural family.

Chemists have more recently been led to inquire whether some of the inorganic acids usually esteemed monobasic, should not be also viewed as bibasic. It has been well remarked, that whilst some acids—as, for instance—nitric acid, always form neutral simple salts, others, of which sulphuric acid may be taken as a type, exhibit a great tendency to form acid and double salts. In fact, every reason which could be urged in favour of the bibasic character of tartaric acid would equally apply to sulphuric acid, excepting that we have no compound analogous to Rochelle salt. The argument is perhaps sufficiently strong even now; but could a double sulphate of potash and soda be prepared, the analogy would be complete; and none, I apprehend, who are accustomed to double the formula of tartaric acid, could refuse to view sulphuric acid also as $2\,HO, S_2O_6$.

It was in the attempt to obtain such a salt that the compound now to be described was discovered.

Having occasion to prepare some salt which should show flashes of light on crystallizing, I followed the method recommended in Gmelin's "Handbook of Chemistry," Vol. I, p. 207. 2 parts of sulphate of potash, and 1 part of chloride of sodium, were fused together; the mass, removed from the crucible, was dissolved in boiling water, filtered, and suffered to cool. The result was very satisfactory. Small crystals separated, each at its formation emitting a luminous flash, visible even in shaded daylight. Their appearance struck me as being very uniform, yet certainly not that of sulphate of potash; and it occurred to me that they might be a double sulphate of the two alkalies. The crystals were examined by Mr. Crosby, of St. Thomas's Hospital, and were found to contain no water, but to give a precipitate with antimoniate of potash. They consisted of about 48 per cent of sulphuric acid, and 47 per cent of potash; the remaining 5 per cent, or thereabouts, being soda. This was quite inconsistent with the formula KO, NaO, S_2O_6; but it might well contain such a compound, mixed with ordinary sulphate of potash.

A series of experiments was set on foot in order to obtain, if possible, pure crystals of this supposed salt. The salts obtained were freed from hygroscopic moisture by heating them; sulphuric acid was determined in the usual way as baryta-salt, and the potash as platinum-salt. Every analysis that was made by me is recorded.

Exp. 1. A crop of large crystals was obtained by the process already described. They were very regular in form—six-sided prisms, terminating in six-sided pyramids, truncated.

Salt employed.	Sulph. baryta obtained.
38·18 grs.	53·10 grs.
27·61 „	38·65 „
Salt employed.	**Chlor. plat. and pot. obtained.**
13·83 grs.	33·32 grs.

The acid and base thus determined are in the proportion:

Sulphuric acid	47·77	and	48·06 per cent
Potash . . .	46·58		„

Now, in order to obtain such numbers as these, we must suppose that 6 equivs. of sulphuric acid are combined with 5 of potash and 1 of soda.

	Equivs.	Calculated.	Average of experiments.
Sulphuric acid	6	47·26	47·91
Potash . . .	5	46·57	46·58
Soda . . .	1	6·16	5·34
		100·00	100·00

Exp. 2. One part of sulphate of potash was mixed with two parts of crystallized sulphate of soda, that is, about equivalent proportions; water was expelled from the mixture by heat, and the salts were fused together. The cooled mass was dissolved in hot water, which presently afforded crystals similar in appearance to the preceding. They were dried and analyzed.

Salt employed.	Salt obtained.
32·64 grs.	45·60 grs. sulph. of baryta.
14·65 „	35·81 „ chlor. plat. pot.

These numbers indicate:

Sulphuric acid	47·96 per cent
Potash . . .	47·26 „

This salt is evidently identical with the preceding.

Exp. 3. One part of sulphate of potash and two parts of crystallized sulphate of soda were dissolved together in water by the aid of heat. There separated on cooling, small crystals, of a perfectly definite appearance, six-sided prisms with six-sided pyramids at the ends, truncated. They were analyzed as before.

Salt employed.	Salt obtained.
10·20 grs.	14·41 grs. sulph. baryta.
8·31 „	19·31 „ chlor. plat. pot.

These numbers indicate:

Sulphuric acid	48·49 per cent
Potash . . .	44·92 „

These results differ but little from those previously obtained.

Exp. 4. A mixture of *equal* parts of sulphate of potash and chloride of sodium fused together and dissolved in hot water, afforded crystals which were evidently the same.

Exp. 5. Three parts of bisulphate of potash and one part of chloride of sodium were fused together. Hydrochloric acid was given off in large quantity, as might be expected; and on dissolving the fused mass in hot water, and suffering it to cool, there separated

hexagonal crystals, apparently identical with those previously examined, mixed with another salt in feathery flakes.

Exp. 6. The same salts, mixed in the same proportions, were boiled together for a considerable time in water. The solution yielded the feathery flakes above mentioned, along with crystals that appeared to be thin segments of hexagonal prisms, but which Dr. Leeson, by a minute examination of their angles, found to be derived from the octagon of the regular system by the development of two of the opposite planes. They were found to contain soda, and no water. On analysis, they yielded the following results:

Salt employed.	Salt obtained.
25·09 grs.	35·12 grs. sulph. baryta.
14·17 „	33·20 „ chlor. plat. pot.

which indicate:

Sulphuric acid	48·05 per cent
Potash . . .	45·29 „

As the microscope showed some small needle-shaped crystals sticking to these octagonal ones, a portion of the salt was washed several times with a very little cold water, and analyzed.

Salt employed.	Salt obtained.
7·51 grs.	10·37 grs. sulph. baryta
6·00 „	14·22 „ chlor. plat. pot.

which indicate:

Sulphuric acid	47·40
Potash . . .	45·83

Another portion of salt was prepared from the same source, recrystallized, and then washed with a little cold water. The crystals were small, but of the same form as the first. They were analyzed.

Salt employed.	Salt obtained.
21·46 grs.	29·61 grs. sulph. baryta
7·23 „	17·49 „ chlor. plat. pot.

which indicate:

Sulphuric acid	47·37 per cent
Potash . . .	46·75 „

All these results seem to point out a salt similar in composition to all those previously examined.

Exp. 7. A saturated solution of carbonate of soda was added to a saturated solution of bisulphate of potash until effervescence ceased.

A crystal or two separated. The solution yielded on evaporation a crop of crystals, bearing a general resemblance to the salt formerly obtained. They were dried and analyzed.

Salt employed.	Salt obtained.
24·42 grs.	33·95 grs. sulph. baryta
12·06 „	27·40 „ chlor. plat. pot.

which indicate:

Sulphuric acid	47·73 per cent
Potash . . .	43·92 „

differing little from previous estimations.

Exp. 8. One part of nitrate of potash and two parts of crystallized sulphate of soda, dissolved together, and evaporated, gave crystals of the compound salt, mixed with nitre.

Exp. 9. In order to see whether the same salt would form in the presence of a large excess of acid, 3 ounces of sulphate of potash, 6 ounces of crystallized sulphate of soda, and nearly 2 fluid ounces of sulphuric acid, were boiled together in water, and evaporated. The crystals, which were small, and of the ordinary shape, were slightly washed with cold water, dried, and analyzed.

Salt employed.	Salt obtained.
27·78 grs.	39·17 grs. sulph. baryta,

which indicates:

Sulphuric acid . .	48·40 per cent.

This scarcely exceeds the previous determinations of sulphuric acid. The salt was evidently the same.

Exp. 10. Conversely, the effect of an alkaline solution was tried. Two parts of sulphate of potash and one part of hydrate of soda were dissolved together in water. The evaporated solution gave a crop of very minute crystals. They were washed with a little cold water two or three times, dried over sulphuric acid, and analyzed.

Salt employed.	Salt obtained.
18·39 grs.	25·61 grs. sulph. baryta,

which indicates:

Sulphuric acid . .	47·81 per cent.

Hence the salt was identical with those analyzed before.

Exp. 11. Thinking that a large excess of soda might cause the formation of a salt richer in soda, 6 parts of that sulphate, crystallized, were dissolved in water with 1 part of sulphate of potash, and evaporated. Crystals of common sulphate of soda alone separated.

On another occasion, when 1 lb. of sulphate of soda had been dissolved along with ½ lb. of sulphate of potash, the solution yielded, first, six-sided prisms, with dihedral summits, containing soda; then large crystals of sulphate of soda; and the mother-liquor from them yielded again a crop of the compound salt.

It appears, then, that all these attempts have failed to produce a sulphate of potash and soda analogous to the double tartrate; but they invariably yielded a compound salt containing a small amount of soda. This has all the appearance of being definite and uniform, and seems to consist of sulphuric acid, combined with 6 equivs. of base, 1 being soda and 5 potash. Its formula decides nothing in favour of the bibasic character of sulphuric acid, but it does not militate against such a view: it may be written 5 KO, NaO, 3 S_2O_6, though perhaps chemists will generally prefer the expression 5(KO, SO_3) + NaO, SO_3.

It may be asked, why was not the salt subjected to repeated crystallizations before it was analyzed? The reason was, that I feared some alteration in the salt during such a process; indeed, a specimen which had thus been treated, was found to have lost 1 per cent of sulphuric acid, showing a considerable decrease in the amount of soda.

Salt employed.	Salt obtained.
26·11 grs.	35·38 grs. sulph. baryta.
25·05 „	34·08 „

which indicate:

Sulphuric acid, 46·52 and 46·70 per cent.

Had the salt been entirely reduced to ordinary sulphate of potash, analysis should have given only 45·94 per cent.

The solubility of this compound salt was found to be very similar to that of sulphate of potash itself: 1000 parts of water at 212° F. were found capable of dissolving 250 parts; at 55° F., 101 parts; and at 40° F., 92 parts of the salt. 25 grs. of salt, recrystallized during this experiment, was found to yield 34·11 grs. of sulphate of baryta, indicating 46·90 per cent of sulphuric acid.

The crystalline form, also, is the same as that of sulphate of potash; but the crystals appeared to me more uniform than that salt ordinarily is, and having not so great a tendency to become long and branching. The compound and the simple salt are both alike anhydrous.

Since performing these experiments, I have consulted the original paper of Rose, in Pogg. LII, "*Ueber die Lichterscheinungen bei*

der Krystallbildung." I find he has accurately described the crystals which emit light, but his quantitative determinations led him to doubt their definite character; I, however, have always found them uniform in composition, in whatever manner they may have been produced. Their production, indeed, under such various circumstances, could not have been anticipated; and they form a remarkable instance of a certain proportion of the base of a salt being replaced by an analogous oxide, without materially affecting its physical properties.

XI.—*Note on Thierschite.*

By J. Liebig.

(from a letter to Dr. Hofmann.)

Some time ago, I received from Dr. F. von Thiersch, General Conservator of the scientific collections of Bavaria, a fragment of a white marble column from the Parthenon, for the purpose of analyzing the incrustation with which the external surface of the column was covered, the chief object of the examination being to decide whether the column had been painted with a colour of a still determinable nature.

The incrustation was about $\frac{1}{20}$ of an inch thick, and possessed the hardness of fluor-spar. Under the microscope, when illuminated by sun-light, it appeared as a lustrous, opaline aggregate of warty nuclei, exhibiting a concentric structure. When seen by the naked eye, it appeared an uneven layer of a dingy-grey colour, covering the whole outer surface of the stone.

A portion of the detached crust dissolved in acetic acid with effervescence; the solution contained nothing but lime. The greater portion was insoluble in acetic acid, but was readily dissolved by nitric acid, only a trifling residue remaining behind.

The nitric solution gave, upon addition of ammonia, a snow-white precipitate, insoluble in ammonia. After addition of acetate of soda, it furnished, with salts of silver and lead, a white precipitate. This deportment pointed towards oxalic acid, and indeed a more minute examination soon convinced me that the chief mass of the incrustation, which had been taken for a pigment used in painting the column, consisted of crystallized oxalate of lime.

I treated the precipitate produced by ammonia in the nitric

solution with chloride of copper, which converted it into a bluish powder, whilst the lime was dissolved. The copper precipitate dissolved readily in ammonia; and this solution yielded, after the copper had been thrown down, a beautiful crystallization of oxalate of ammonia which was decomposed, without deposition of carbon, into carbonic acid and carbonic oxide when heated with concentrated sulphuric acid, and from which oxalic acid, with all its properties, was prepared in sufficient quantity for an analysis, if such had been considered necessary.

Dr. Sendtner, Adjunct to the Botanical Gardens in Munich, who has a great deal of experience in researches of this kind, was unable to discover any organic structure, either in the incrustation itself or in the residue insoluble in nitric acid. I believe, therefore, I am justified in considering this incrustation, which will probably be found upon many lime-stones, as a mineral species; and since Sandall has observed crystallized oxalate of lime between metastatic calc-spar crystals in Hungary, without proposing a mineralogical name for it, I have great pleasure in coupling with this mineral the name of the learned man whose labours have so successfully contributed to the elucidation of antiquities, and who has given rise to the present observations.

The origin of this oxalate of lime can scarcely be doubtful; it is evidently derived from lichens vegetating upon the lime-stone; it is the residue of a series of generations, following each other during centuries, until the whole surface of the stone—in consequence of the gradual destruction of former vegetations, whose organic matter decayed, while the oxalate of lime produced during their vitality remained unaltered—was so completely covered, that new germs of lichens no longer found the soil of carbonate of lime necessary for their development. The residue of the incrustation, insoluble in nitric acid, when heated in a glass tube, was slightly charred; it contained traces of a humus-like substance, evidently the last residue of the lichens, protected by the oxalate of lime from entire destruction.

XII.—*On Kyanurenic Acid.*

By J. Liebig.

(from a letter to dr. hofmann).

During some experiments made by Professor Bischoff, regarding the amount of uric acid in dog's urine, the latter was very frequently

examined for uric acid. In no case could a trace of this acid be detected.

During these researches, the urine deposited sometimes, but not very frequently, a precipitate which, on account of its minute divisions, was difficult to filter. An examination of this deposit has proved that it consists chiefly of a new acid which I propose to call *kyanurenic acid*, in order to remind us of its origin.

On dissolving the coloured deposit of dog's urine in lime-water, diluting with water, and adding hydrochloric acid to the gently warmed liquid, kyanurenic acid separates in delicate colourless needles which, on drying, become very light, and assume a satiny lustre; they redden blue litmus-paper. From concentrated solutions the acid is deposited in the form of a powder. When heated in a glass tube, the acid fuses to a brown liquid which on further application of heat sublimes, a trace of charcoal remaining behind. The sublimate is white satiny lustrous crystalline; it dissolves in alcohol, and differs by this deportment from the original acid. Kyanurenic acid may be readily distinguished from uric acid by its solubility in hydrochloric acid; the precipitate which is produced in alkaline solutions of the acid, upon addition of hydrochloric acid, disappears again, if an excess be added. It dissolves readily in boiling hydrochloric acid, and in dilute sulphuric and nitric acid; in the latter, apparently without decomposition. Its hot saturated solutions solidify, upon cooling, to a magma of short, extremely lustrous needles. In cold concentrated sulphuric acid, kyanurenic acid dissolves without change; on gently warming, the solution assumes a light-brown colour, and now deposits, upon addition of water, a beautiful lemon-yellow, amorphous precipitate which is sometimes mixed with crystals of unchanged acids. Kyanurenic acid readily dissolves in the caustic, and, upon application of heat, also in the carbonated alkalies, also in lime- and baryta-water; when employed in sufficient quantity, it perfectly destroys their alkaline reaction. Evaporation of these solutions yield well crystallized salts. The lime-salt forms stellar groups of short hard needles; the baryta-salt, feather-like, united leaflets, exhibiting the lustre of mother-of-pearl: both salts are difficultly soluble in water. A solution of the acid in ammonia furnishes, upon addition of nitrate of silver, a dense, white precipitate, insoluble in hot water.

I have abstained from sacrificing to an elementary analysis the small portion of this substance which I had at my disposal, inasmuch as the composition of this body which seems to occur but rarely, and in small quantities, appeared to me less important than the

proof of its existence, and the study of those properties by means of which it may be readily recognized again. According to the experiments which I have made, kyanurenic acid contains no nitrogen, or only so small a quantity that the minute portions which I was able to devote to the experiments were insufficient to show its presence.

XIII.—*Analysis of the Waters from the Deep Wells of Westbourne Park and Russell Square, and the Artesian Well of the Hanwell Lunatic Asylum.*

By Charles Harwood Clarke, Esq., B.A., F.S.A., and Henry Medlock, Esq., F.C.S.

The deep well of Westbourne Park is situated a short distance to the north of Westbourne Grove. It was sunk several years since by J. W. Treeby, Esq., for the purpose of supplying the houses on his private estate. The surface of the ground in the neighbourhood is 73·5 feet above the Ordnance datum line. The depth of the well is 230 feet, and the water rises to within 120 feet of the surface. It is sunk through various strata of sand and clay, and a bore-pipe carried to a depth of 15 feet into the chalk. The supply of water is derived from two strata, the chalk, and the sand immediately above it. The samples for analysis were collected in December, 1852, the one (*A*) being taken from the well, and the other (*B*) from the bore-pipe which leads into the chalk. Both specimens were bright and colourless, and possessed an agreeably refreshing but slightly saline taste.

At the time the water was collected, the bore-pipe had been closed, and the sample (*A*) was considered as being derived exclusively from the sand strata immediately above the chalk.

The quantitative analysis yielded the following results:

A. Determination of the total quantity of fixed constituents.

Water employed.	Residue obtained (dried at 120° C. = 248° F.)	Percentage.
44520 grs.	36·3744 grs.	0·081703

B. Determination of organic matter.

Water employed.	Organic matter expelled at a dull red heat.	Percentage.
44520 grs.	0·4573 gr.	0·001027

C. Determination of silicic acid.

Water employed.	Silicic acid obtained.	Percentage.
44520 grs.	0·4152 gr.	0·000932

D. Determination of iron, alumina and phosphates.

Water employed.	Precipitate obtained.	Percentage.
44520 grs.	0·2185 gr.	0·000490

E. Determination of lime.

Water employed.	Carbonate of lime obtained.	Percentage of lime.
44520 grs.	2·2246 grs.	0·002798

F. Determination of magnesia.

Water employed.	Pyrophosphate of magnesia obtained.	Percentage of magnesia.
44520 grs.	1·7817 grs.	0·001451

G. Determination of chlorine.

Water employed.	Chloride of silver obtained.	Percentage of chlorine.
70000 grs.	43·4695 grs.	0·015351

H. Determination of sulphuric acid.

Water employed.	Sulphate of baryta obtained.	Percentage of sulphuric acid (SO_3).
70000 grs.	39·0852 grs.	0·019170

I. Determination of alkalies.

Water employed.	Mixed chlorides obtained.
70000 grs.	46·4693 grs.

a. Determination of potassium.

Water employed.	Bichloride of platinum and chloride of potassium obtained.	Percentage of potassium.
70000 grs.	55·0502 grs.	0·012559

b. Determination of sodium.

Water employed.	Chloride of sodium obtained.	Percentage of sodium.
70000 grs.	29·6747 grs.	0·016667

J. Determination of carbonic acid:

In order to obtain a perfectly fresh sample of the water for the determination of the carbonic acid, the well was pumped nearly to dryness and the water collected as it issued rapidly from the strata of sand. A bottle containing ammonia and solution of chloride of calcium, and capable of holding in addition 70000 grs. of water, was

filled, and the precipitated carbonate of lime subsequently determined.

Water employed.	Precipitate of carbonate of lime obtained.	Percentage of carbonic acid.
70000 grs.	39·0909 grs. containing 17·2004 grs. of carbonic acid.	0·024572

The second sample of water (*B*) was taken from the bore-pipe which passes to a depth of 15 feet into the chalk, and was supposed to be derived exclusively from the chalk strata below the sand. The following results were obtained by quantitative analysis.

A. Determination of the total quantity of the fixed constituents.

Water employed.	Residue obtained (dried at 120° C. = 248° F.)	Percentage.
44520 grs.	36·0498 grs.	0·080973

B. Determination of organic matter.

Water employed.	Organic matter expelled at a dull red heat.	Percentage.
44520 grs.	0·6683 gr.	0·001500

C. Determination of silicic acid.

Water employed.	Silicic acid obtained.	Percentage.
44520 grs.	0·3003 gr.	0·000673

D. Determination of iron, alumina and phosphates.

Water employed.	Precipitate obtained.	Percentage.
44520 grs.	0·3973 gr.	0·000892

E. Determination of lime.

Water employed.	Carbonate of lime obtained.	Percentage of lime.
44520 grs.	2·1364 grs.	0·002710

F. Determination of magnesia.

Water employed.	Pyrophosphate of magnesia obtained.	Percentage of magnesia.
44520 grs.	1·4630 grs.	0·001191

G. Determination of chlorine.

Water employed.	Chloride of silver obtained.	Percentage of chlorine.
44520 grs.	26·5804 grs.	0·014755

H. Determination of sulphuric acid.

Water employed.	Sulphate of baryta obtained.	Percentage of sulphuric acid (SO_3).
44520 grs.	23·9932 grs.	0·018502

I. Determination of alkalies.

Water employed.	Mixed chlorides obtained.
44520 grs.	28·9235 grs.

a. Determination of potassium.

Water employed.	Bichloride of platinum and chloride of potassium obtained.	Percentage of potassium.
44520 grs.	37·3976 grs.	0·013415

b. Determination of sodium.

Water employed.	Chloride of sodium obtained.	Percentage of sodium.
44520 grs.	17·5143 grs.	0·015467

J. Determination of carbonic acid.

The water was taken direct from the bore-pipe, and introduced immediately into the bottle containing ammonia and chloride of calcium.

Water employed.	Precipitate of carbonate of lime obtained.	Percentage of carbonic acid.
70000 grs.	38,8218 grs. containing 17·0816 grs. of carbonic acid.	0·024402

The deep well in Russell Square is situated on the north side of the square. The surface of the ground is 82 feet above the Ordnance datum line. The well is sunk through the sand, and a bore-pipe carried to a depth of 100 feet into the chalk. The total depth of the well is 230 feet, and the water rises to within 130 feet of the surface, differing in height only by a few inches from the level of the water in the well at Westbourne Park.

The sample for analysis was collected in December, 1852, and gave the following results:

A. Determination of the total quantity of fixed constituents.

Water employed.	Residue obtained (dried at 120° C=248° F.)	Percentage.
44520 grs.	30·3701 grs.	0·068213

B. Determination of organic matter.

Water employed.	Organic matter expelled at a dull red heat.	Percentage.
44520 grs.	0·5005 gr.	0·001098

C. Determination of silicic acid.

Water employed.	Silicic acid obtained.	Percentage.
44520 grs.	0·5112 gr.	0·001148

D. Determination of iron, alumina, and phosphates.

Water employed.	Precipitate obtained.	Percentage.
44520 grs.	0·1694 gr.	0·000380

E. Determination of lime.

Water employed.	Carbonate of lime obtained.	Percentage of lime.
44520 grs.	14·3220 grs.	0·001801

F. Determination of magnesia.

Water employed.	Pyrophosphate of magnesia obtained.	Percentage of magnesia.
44520 grs.	0·5852 gr.	0·000472

G. Determination of chlorine.

Water employed.	Chloride of silver obtained.	Percentage of chlorine.
44520 grs.	20·0015 grs.	0·011106

H. Determination of sulphuric acid.

Water employed.	Sulphate of baryta obtained.	Percentage of sulphuric acid (SO_3).
44520 grs.	19·7274 grs.	0·015213

I. Determination of alkalies.

Water employed.	Mixed chlorides obtained.
44520 grs.	26·2831 grs.

a. Determination of potassium.

Water employed.	Bichloride of platinum and chloride of potassium obtained.	Percentage of potassium.
44520 grs.	20·7468 grs.	0·007458

b. Determination of sodium.

Water employed.	Chloride of sodium obtained.	Percentage of sodium.
44520 grs.	19·9537 grs.	0·017620

J. Determination of carbonic acid.

Water employed.	Carbonate of lime obtained.	Percentage of carbonic acid.
50640 grs.	26·9546 grs. containing 11·8600 grs. of carbonic acid	0·023420

The artesian well at Hanwell is sunk near to, and supplies the Asylum. The depth of the well is 235 feet, and the water rises to a height of 36 feet above the surface, the level of the ground being 74·5 feet above the Ordnance datum line.

The sample submitted to analysis was collected in February last, and gave the following results:

A. Determination of the total quantity of fixed constituents.

Water employed.	Residue obtained (dried at 120°C = 248° F.)	Percentage.
44520 grs.	30·4350 grs.	0·068514

B. Determination of organic matter.

Water employed.	Organic matter expelled at a dull red heat.	Percentage.
44520 grs.	1·1473 grs.	0·002719

C. Determination of silicic acid:

Water employed.	Silicic acid obtained.	Percentage.
44520 grs.	0·1155 gr.	0·000259

D. Determination of iron, alumina and phosphates:

Water employed.	Precipitate obtained.	Percentage.
44520 grs.	0·2046 gr.	0·000459

E. Determination of lime:

Water employed.	Carbonate of lime obtained.	Percentage of lime.
44520 grs.	3·2725 grs.	0·00411

F. Determination of magnesia:

Water employed.	Pyrophosphate of magnesia obtained.	Percentage of magnesia.
44520 grs.	3·9270 grs.	0·003196

G. Determination of chlorine:

Water employed.	Chloride of silver obtained.	Percentage of chlorine.
44520 grs.	15·4693 grs.	0·008588

H. Determination of sulphuric acid:

Water employed.	Sulphate of baryta obtained.	Percentage of sulphuric acid (SO_3).
44520 grs.	19·7967 grs.	0·015266

I. Determination of alkalies:

Water employed.	Mixed chlorides obtained.
44520 grs.	22·2607 grs.

a. Determination of potassium:

Water employed.	Bichloride of platinum and chloride of potassium obtained.	Percentage of potassium.
44520 grs.	35·8204 grs.	0·012845

b. Determination of sodium:

Water employed.	Chloride of sodium obtained.	Percentage of sodium.
44520 grs.	11·3328 grs.	0·008666

J. Determination of carbonic acid:

Water employed.	Carbonate of lime obtained.	Percentage of carbonic acid.
50640 grs.	33·6767 grs. containing 14·8177 grs. of carbonic acid.	0·029605

From the above analyses we have deduced the following results: In Table I, the constituents, as found by analysis, are given separately, and in Table II, the acids and bases are associated in the usual manner:

TABLE I.

	Westbourne water. A. Sand.	Westbourne water. B. Chalk.	Russell Square water.	Hanwell water.
	Grains in an imperial gallon.			
Lime	1·9588	1·8972	1·2611	2·8813
Magnesia	1·0159	0·8341	0·3307	2·2376
Potassium	8·7918	9·3909	5·2096	8·9919
Sodium	11·6670	10·8271	12·3342	6·0665
Iron, alumina and phosphates	0·3430	0·6247	0·2663	0·3217
Sulphuric acid (SO_3)	13·4195	12·9514	10·6491	10·6861
Chlorine	10·7461	10·3287	7·7746	6·0121
Carbonic acid	17·2004	17·0816	16·3941	20·4824
Silicic acid	0·6529	0·4712	0·8037	0·1817
Organic matter	0·7191	1·0502	0·7690	1·8033

TABLE II.

	Westbourne water. A. Sand.	Westbourne water. B. Chalk.	Russell Square water.	Hanwell water.
	Grains in an imperial gallon.			
Carbonate of lime	3·4978	3·3878	2·2519	5·1451
„ magnesia	2·1223	1·7425	0·6908	4·6746
Chloride of sodium	17·7083	17·0205	12·8116	9·9072
Sulphate of soda	8·2148	5·7733	9·4181	2·5980
Carbonate of soda	4·7100	5·2200	9·7261	3·0642
Sulphate of potassa	19·1220	21·0949	11·6213	20·0590
Silicic acid	0·6529	0·4712	0·8037	0·1817
Iron, alumina and phosphates	0·3430	0·6247	0·2663	0·3217
Organic matter	0·7191	1·0502	0·7690	1·8033
Total	57·0895	56·3851	48·3588	47·7548
Solid residue obtained on evaporation	57·1927	56·6812	47·7511	47·9600
Free carbonic acid (grains in a gallon)	12·5830	12·5185	11·0060	12·7174
Free carbonic acid (in cubic inches at 44° F.)	25·1660	25·0370	22·0120	25·4348
Degree of hardness, Clark's scale — before boiling	6°·5	5°·6	4°·3	12°·1
Degree of hardness, Clark's scale — after boiling	0°·7	0°·5	0°·9	1°·4

A striking feature in the foregoing analyses is the almost complete identity of the water from the sand and that from the chalk in the well at Westbourne Park. This circumstance proves that the so-called chalk-water supply to the deep wells of London is not entirely confined to that stratum.

The great similarity between the Westbourne and Russell Square waters, and the levels at which they stand in the wells being the same, show that both wells are supplied by the same water-stratum. These waters also agree very closely in composition with the water of Trafalgar Square.*

On comparing the analysis of the Hanwell water with those of the deep well-waters of London, the difference between them is comparatively trifling, showing an evident connection between them, notwithstanding the great difference of level at which the Hanwell water stands as compared with the wells of London. This would seem to indicate the existence of a basin to the west of London, the water in which stands at a much higher level than the water under London, and from the overflowing of which the deep wells of the metropolis derive a considerable portion of their supply. We are indebted for this suggestion to Mr. Henry Marten, who examined the district for the West London Water Works Company.

The analyses hitherto made of the deep well-waters of London and the neighbourhood, are not sufficiently numerous to admit of any definite conclusion being drawn as to the probable sources of the water supply. We have been induced, however, to communicate the results of our analyses to the Society as an additional contribution to a knowledge of the deep well-waters of London.

XIV.—*On the increase in Weight of Molasses casks occasionally arising from Absorption.*

By William Ferguson, Esq., F.C.S.

In September, 1851, attention was attracted to an unusual increase of weight in a shipment of molasses, which occurred in the London Docks; it was some time before the cause could be discovered, and the steps taken to ascertain it ended in the perfect assurance that it

* Quart. Journ. Ch. Soc. I, 97.

was due to absorption. The great extent to which the action had taken place, and the large amount of property in our dock warehouses which is thus proved to be occasionally affected by it, lead me to believe that a detailed account of this extraordinary instance may prove acceptable to the Society. For the following particulars I am indebted to Mr. Muggeridge, of the London Docks, in whose care the molasses were stored, and by whom the progress of the action was watched.

In August, 1849, a quantity of molasses were housed for the first time in a damp cellar, where they lay until September, 1851, when the increase of weight was observed. In order to ascertain its amount, the whole of the casks of the importation were re-weighed, when it was found that every cask which had not lost a portion of its contents by breakage, had gained considerably in weight. The casks were coopered and made tight, and in February, 1852, were again weighed, when (where breakage had not occurred) a further increase was found to have taken place. The total weight of the shipment was 1270 cwt. It was stored in 110 casks, containing from 11 to 12 cwt. each. The increase on different casks varied considerably, reaching in some cases 38 lbs. or about 3 per cent of the contents. The total observed increase was $23\frac{1}{4}$ cwt., or about 1·83 per cent. This does not represent the total real increase, for it would appear that in some casks the absorbed water had just been sufficient to cover the loss from breakage, but not tell as increase; and there does not seem to have been one cask which had not suffered more or less loss. The real increase of weight due to absorption must have been much greater than that shown by the weighings. Important as this result was to the merchant, it was greatly exceeded by one that was afterwards observed, and which was as follows. A quantity of molasses imported in large tanks were, in July, 1849, racked into 347 puncheons, weighing about 12 cwt. each, the total weight being 4160 cwt.; they were stowed in a lofty cellar, where they remained till September, 1852, when they were re-weighed for delivery. At various times some of the casks were found with heads bulging out from internal pressure, although none of them were full when housed, and it was necessary to draw off a portion to prevent them from bursting. When the bung was started, the molasses rushed out with great force, ascending several feet to the roof of the cellar. On re-weighing, the increase was, as before, found to be different in different casks. On 52 there was a loss from breakage, 248 had gained from 1 lb. to 30 lbs. each, 67 from 30 lbs. to 40 lbs., and 20

from 40 lbs. to 51 lbs. each. The total increase of weight on the shipment was 56 cwt. If we take the casks on which this increase took place, laying aside the 52 on which there was loss, the excess of absorbed water over the leakage was about 1·6 per cent; in some of the casks it had reached as high a percentage as 4·25. A third case was also observed in December, 1848. 500 puncheons were filled from tanks in which they had been imported, and stored in the same cellar till July, 1852, when some of them were re-weighed with the same various results as to increase: 5 puncheons gave the following results:

No. 1,	weight	11	3	13	lbs.	gained	23	lbs.
„ 2,	„	11	1	7	„	„	31	„
„ 3,	„	12	0	7	„	„	40	„
„ 4,	„	11	2	0	„	„	45	„
„ 5,	„	12	0	0	„	„	68	„

This was the largest increase of weight, though on a large number of casks it reached nearly to the same percentage. In No. 5 the excess of water absorbed over any leakage that may have occurred is 5 per cent. The bungs were at this time started, and the casks, which had been stored not quite full, were found full to overflowing. One cask which had lost 14 lbs., and another 9 lbs., were also full, We know that these casks had not been overdrawn. Now, to effect a loss of 14 lbs., 4 gallons of treacle must have been replaced by water, not taking into account the quantity which was required to fill the cask completely. In the case of No. 5, where the increase of weight was 68 lbs., the quantity of water absorbed must have been very great, for after supplying the loss due to leakage, (and all casks leak more or less), 6·8 gallons of water entered through the pores of the wood during a period of 3½ years. These puncheons, in which this maximum effect took place, had been American meal-casks, made of Quebec timber, which is much more porous than the wood of which West India puncheons are usually made. The specific gravity of the freshly-imported molasses of the last lot was 1·394, and when taken in July, 1852, was 1·375.

XV.—*On some New Basic Products obtained by the Decomposition of Vegetable Alkaloids.*

By Henry How, Esq., F.C.S.

ASSISTANT TO PROFESSOR ANDERSON, OF GLASGOW.

In the following pages, I purpose submitting to the notice of the Society the results of some experiments, so far as I have proceeded with them, on the action of the halogen-compounds of the alcohol radicals on bases of vegetable origin. The beautiful researches of Hofmann on the behaviour of artificial liquid bases and of ammonia, under these circumstances, led him to remark that a similar course of investigation, in regard to basic substances generally, would no doubt tend to throw much light on the nature of these bodies. On comparing the formulæ of some of the vegetable alkaloids with which I was best acquainted, their relations to each other were such that I was curious to bring to light the result of experimenting upon some of these substances in the direction mentioned.

The established formula for morphia, which was first given as the correct interpretation of the analysis of the pure alkaloid by Laurent,* and which I have confirmed by experiments of my own, is

$$C_{34}H_{19}NO_6.$$

It will be seen, by a comparison of this formula with that of codeine, as established beyond a doubt by Professor Anderson,†

$$C_{36}H_{21}NO_6,$$

that these alkaloids differ from each other exactly by C_2H_2. Now, reasoning from analogy, if these bases follow the same laws of decomposition as their volatile congeners, I should, by the action of iodide (*e. g.*) of methyl upon morphia, obtain either codeine or a base having the same centesimal composition, according to the reaction expressed in the equation:

$$C_{34}H_{19}NO_6 + C_2H_3I = C_{36}H_{21}NO_6 = C_{34}\left\{\begin{matrix}H_{19}\\C_2H_2\end{matrix}\right\}NO_6 + HI.$$

It was with this idea that I commenced the following series of experiments; and although the reaction represented above was not that which I studied first—for iodide of ethyl was ready to my hand—the results which I obtained with this compound, though not such as to render me sanguine as to the actual conversion of the one

* Ann. Ch. Phys. [3], XIX. † Trans. Roy. Soc. Edinb. XX, I, 57.

alkaloid into the other—a problem which has engaged the attention of chemists of great name*—were sufficiently marked in character to urge me to prosecute the inquiry, with what success will be seen in the sequel.

If, in the succeeding pages, the numbers given in one or two instances fall somewhat below the standard of accurate analytical proof, I trust that, to those acquainted with the nature of the materials employed, the mention of their costly character will be sufficient excuse for a want of repetition of experiments where a great deal would not have been gained by the same; believing that sufficient evidence is furnished as to the composition at least of the substances produced. I beg here to offer my most sincere thanks to Professor Anderson, in whose laboratory, attached to the University of Glasgow, my experiments were performed, for the opportunity of conducting this inquiry.

In detailing the investigation, I have preferred to narrate the individual reactions, &c., in the order in which they were examined.

ACTION OF IODIDE OF ETHYL UPON MORPHIA.

Morphia, in a state of fine powder, was introduced into a combustion-tube, strongly sealed at one end, a little iodide of ethyl added, and then absolute alcohol, in quantity judged to be sufficient to dissolve the alkaloid. I found about 25 grains might be conveniently employed in a tube of small bulk; and alcohol occupying about three times the space of the alkaloid was found sufficient, a very small quantity of iodide of ethyl being required. When the substances were all introduced, the tube was carefully sealed before the blow-pipe, and upon its cooling, the whole was immersed in boiling water. Complete solution took place when a small quantity of morphia was employed, but not so when more was used; action commenced very speedily, as was obvious from the nature of the solid product in the tube, which had not the appearance of morphia. The boiling was continued some hours when complete solution had not taken place at first, in order that any morphia which had at first remained undissolved might in its turn be acted upon, as the alcohol became free, as it were, by deposition of the new product. When the action had continued about six hours or so, the tube was allowed to cool, and then opened; the alcohol containing the excess of iodide of ethyl, nearly colourless and quite limpid, was poured off from the white crystalline solid product, which was then washed with a little

* Ann. Ch. Pharm. XXVI, 60.

alcohol, and dried. It was found to dissolve readily in hot water; accordingly, the whole was treated in this manner, in case of any morphia remaining unattacked, from which, it being insoluble or very difficultly soluble in this menstruum, the product would by this means be purified. However, complete solution took place; and the fluid deposited, on cooling, a substance in fine white needles; these were collected, dried and analyzed, a preliminary experiment having shown that they contained much iodine.

In the following analysis, the iodine was determined by direct precipitation of an aqueous solution by nitrate of silver; the combustion made with chromate of lead:

5·155 grs., dried at 212°, gave
9·725 „ carbonic acid, and
2·665 „ water.
4·470 „ gave
2·365 „ iodide of silver.

	Experiment.	Calculated.		
Carbon . .	51·45	51·71	C_{38}	228
Hydrogen .	5·74	5·44	H_{24}	24
Nitrogen .		3·17	N	14
Oxygen .		10·87	O_6	48
Iodine . .	28·59	28·81	I	127·1
		100·00		441·1

A comparison of the experimental numbers with the calculation appended, will show that we have here a substance which may be termed the hydriodate of ethylomorphia, and whose constitution may be represented by the formula,

$$C_{34}\left\{\begin{matrix} H_{18} \\ C_4H_5 \end{matrix}\right\}NO_6, HI,$$

an atom of hydrogen of the original alkaloid being replaced by an atom of ethyl in the production of the new base, according to the equation,

$$C_{34}H_{19}NO_6 + C_4H_5I = C_{38}H_{23}NO_6, HI = C_{34}\left\{\begin{matrix} H_{18} \\ C_4H_5 \end{matrix}\right\}NO_6, HI.$$

The above salt is the only product of this decomposition, and the entire morphia is transformed into it: in the air-dry state, as crystallized from water, it contains an equivalent of water, which it loses at 212°.

{9·805 grs. air-dry, lost in the water-bath
{0·195 „ water.

The percentage calculated from this result is 1·98, and 1·98 is that corresponding with the formula:

$$C_{38}H_{23}NO_6, HI + aq.$$

Hydriodate of ethylomorphia is difficultly soluble in absolute alcohol, more easily so in rectified spirit: readily dissolved by hot water, from which it is deposited on cooling in brilliant colourless crystals, which magnifying power shows to be flattened prisms: it is not altered in the air.

Neither potash nor ammonia yielded a precipitate with an aqueous solution of this salt; but, before attempting to isolate the base which this fact pointed out would have to be sought in another way, I attempted to control the above formula by an analysis of a platinum-salt, but was unsuccessful. A saturated aqueous solution of hydriodate of ethylomorphia was converted into hydrochlorate by the successive employment of nitrate of silver and hydrochloric acid, and to the clear aqueous solution so obtained, bichloride of platinum was added; no precipitate was formed: a mixture of strong alcohol and ether was added to a small quantity of this solution, and it and the remaining aqueous fluid were allowed to stand during a night; in the morning the former fluid had deposited beautiful tufts of brilliant yellow needles which, though small, were seen when magnified to be well-defined groups of prismatic crystals, while at the bottom of the larger aqueous liquid was an amorphous yellow sediment; this was collected and burned in the usual way, but the resulting percentage of platinum was 2·5 too high to correspond with the theory. I look upon this as an effect of decomposition; and in this respect the new base seems to bear a close analogy with its parent alkaloid, which I have found very prone to change in contact with an excess of bichloride of platinum.

In order to obtain the base, a quantity of the crystallized hydriodate was dissolved in water gently heated, and oxide of silver gradually added till it was in excess. The fluid remained colourless so long as hydriodate was present, but instantly a decided excess of oxide of silver prevailed, dark streaks appeared, and upon filtration a highly caustic liquid was obtained, of a red-brown colour; this deposited no crystals upon cooling, or upon concentration, and when the whole was evaporated to complete dryness at 212°, a semi-transparent, solid, very dark-coloured residue was obtained.

This residue was found to be difficultly soluble in strong alcohol

(90 per cent), and a boiling solution deposited a substance amorphous to the naked eye, but revealing under the microscope distinct crystalline structure; it was scarcely altered in appearance by exposure to the air; but upon adding hydrochloric acid to a portion so exposed, it was observed to dissolve with slight but distinct effervescence to a yellow fluid, which gave a heavy yellow precipitate with chloride of platinum. It was readily and completely soluble in cold water to a red-brown fluid, which exhibited the following behaviour with various re-agents: with bichromate of potash a fine heavy yellow precipitate, soluble in hydrochloric acid; the acid solution became speedily green upon heating from reduction of the chromic acid;—with sulphate of copper a green, with acetate of lead a white, and in excess with nitrate of silver a black precipitate. The latter precipitate, upon the fluid in which it had been formed being heated, gave a slight metallic mirror, and was found to be not completely soluble in ammonia, showing that the base had been oxidized at the expense of the oxide of silver. When it was added to an aqueous solution of sesquichloride of iron, the latter assumed a green colour, darkening to an almost black fluid, with a larger quantity of the alkaline solution, and it was then found to give a blue precipitate with ferridcyanide of potassium, from which fact it is plain, that in this instance also the base had undergone oxidation: ammonia was evolved on heating solution of chloride of ammonium with the alkaline fluid.

Consideration of the foregoing reactions did not permit me to hope for a successful analysis of the alkaline residue, as the pure ethylomorphia; however I made the attempt:

$$\left\{\begin{array}{l} 4{\cdot}040 \text{ grs. dried at } 212^{0}, \text{ gave} \\ 10{\cdot}130 \text{ ,, carbonic acid, and} \\ 2{\cdot}505 \text{ ,, water.} \end{array}\right.$$

The percentages calculated from these numbers, I place in juxtaposition with the required values for the base:

	Experiment.	Calculated for ethylomorphia.		
Carbon . .	68·38	72·84	C_{38}	228
Hydrogen .	6·88	7·34	H_{33}	23
Nitrogen .		4·47	N	14
Oxygen .		15·35	O_6	48
		100·00		313

and the conclusion I draw from the comparison is, that the ethylomorphia I subjected to analysis had already undergone partial oxi-

dation from contact with oxide of silver. I cannot at present add anything to this imperfect history, for my material was exhausted in the experiments described, but sufficient is shown, I think, to make future inquiry of interest. It is obvious the base is extremely prone to decomposition by oxidizing agents; in this character it also resembles its parent morphia, but it shows the tendency in a more marked degree.

I did not attempt to continue the ethylation in this case, a trial of the kind being made with the methyl-product to be next described.

ACTION OF IODIDE OF METHYL UPON MORPHIA.

Morphia was submitted to the action of iodide of methyl under precisely the same circumstances as have been described with reference to iodide of ethyl; after about half an hour's boiling, the change appeared complete, a heavy white crystalline powder, occupying a larger space than the original alkaloid, being formed. The fluid remained almost colourless, and drained away readily from the new product when the tube was opened.

The product was found to dissolve readily in hot water, showing that complete change had taken place. As the water cooled, a deposit was quickly formed in fine brilliant, square, prismatic, colourless needles, of high refractive power. A portion was analyzed in the same manner as the former product:

4·455 grs. dried at 212° gave
8·245 „ carbonic acid, and
2·152 „ water.
4·335 „ give
2·380 „ iodide of silver.

	Experiment.	Calculated.		
Carbon	50·47	50·57	C_{36}	216
Hydrogen	5·36	5·15	H_{22}	22
Nitrogen		3·27	N	14
Oxygen		11·26	O_6	48
Iodine	29·66	29·75	I	127·1
		100·00		427·1

These results point to a decomposition precisely analogous, as was to be anticipated, to the one with iodide of ethyl; the hydriodate of methylomorphia being formed according to the equation

$$C_{34}H_{19}NO_6 + C_2H_3I = C_{36}H_{21}NO_6HI = C_{34}\left\{\begin{matrix}H_{18}\\C_2H_3\end{matrix}\right\}NO_6HI.$$

The salt in the crystallized state contans 2 equivs. of water which it loses at 212°.

9·630 grs. lost on drying in the water-bath
0·400 „ water.

The percentage calculated from this number is 4·15; and 4·04 is that which corresponds to the formula

$$C_{36}H_{21}NO_6 + 2\,HO.$$

This is precisely the formula found for the hydriodate of codeine as dried at 212°, by Professor Anderson;* so that the air-dry hydriodate of methylomorphia is identical in composition with the corresponding salt of codeine as dried at 212°; the salts, however, are only isomeric, for nothing could be more unlike the fine crystalline alkaloid codeine, than the alkaline substance obtained by the action of oxide of silver upon the hydriodate of the new base. In short, it resembles in every particular the corresponding ethyl-compound in appearance and reactions so closely, that to describe them would be to repeat what has been said of that substance. I did not attempt an analysis of this base, but having obtained some in the dry state, proceeded to try the further action of iodide of methyl upon it.

With this view, the base was separated by the action of oxide of silver, of which an excess was attempted to be avoided, on the hydriodate, and subsequent evaporation of the caustic aqueous fluid, which was coloured reddish-yellow, to dryness at 212°; in this state it presented an appearance as beforesaid, exactly similar to that of ethylomorphia, produced by the same means, namely, that of a dark-brown, semi-transparent, amorphous mass. Its reactions were identically those of the former base. The methylomorphia so obtained had most probably commenced to undergo partial oxidation, but as this was unavoidable, the whole was powdered and placed in contact with iodide of methyl and alcohol. Action commenced even in the cold; for on shaking together the contents of the vessel, the fluid became filled with a light-brown flocky substance, which upon trial gave a precipitate with nitrate of silver, showing the presence of hydriodic acid. To ensure reaction, the tube containing the mixture was sealed, and subsequently placed in water at 212°; upon this a resinous substance was immediately formed at the bottom of the tube, and the supernatant liquid became quite clear, the flocky matter disappearing. The heating was continued about half an hour, and no further change taking place in appearance, the tube was allowed

* Trans. Roy. Soc. Edinb. XX.

to cool; a very slight deposit appeared adhering to the sides of the tube, of rather a resinous nature. The tube was opened, and the clear fluid poured from the resin; water was added to it, no change produced; the aqueous fluid was then distilled, to separate the excess of iodide of methyl, and subsequently evaporated at 212°; the residue left was a black amorphous mass, which was found to dissolve only partially in water to a very dark fluid, while a considerable portion remained in the form of a black powder; this proved to be insoluble in every menstruum, with the exception of strong nitric acid, which gave a reddish-yellow solution, nitrous acid being evolved. The watery fluid contained a hydriodate of a base; the quantity being very small, I attempted to obtain some idea of the change effected by converting it into a platinum-salt, carefully avoiding an excess of platinum-solution. I obtained a yellow curdy salt, but in very small quantity, and on determining the percentage of platinum with the utmost care I obtained 21·14 per cent, which is far above that required by the platinum-salt of even morphia itself.

The resinous deposit which was described as adhering to the sides of the tube, appears to be identical with the substance contained in the alcoholic fluid; at least it furnished a solution in hot water, which upon evaporation at 212°, left a residue agreeing in its characters and qualitative reactions precisely with that left by drying up the spirituous liquid; its quantity was too small to admit of quantitative experiments.

I do not venture to draw any definite conclusions from these facts with regard to the continued action of iodide of methyl upon methylomorphia, but that a decomposition of a more complicated nature than the simple assumption of another equivalent of ethyl takes place is, I think, obvious. It will be shown presently that this conclusion seems to be warranted by a deportment of a similar nature observed in reference to a basic product derived from codeine. Further experiment, however, must decide the nature of these changes.

REACTION BETWEEN MORPHIA AND CHLORIDE OF AMYL.

Morphia was placed in contact with chloride of amyl under circumstances precisely similar to those which have been mentioned with regard to iodide of ethyl and methyl. No change took place after three days; for upon opening the tube, the alkaloid was found unaltered. Knowing the reactions of this member of the alcohol series to be somewhat sluggish, I repeated the experiment, expecting a longer exposure to heat might be requisite to effect a decomposition.

Accordingly, a tube was sealed as before, and the contents were kept boiling constantly for about fourteen days. In about four or five days, a crystalline substance began to be formed, and upon opening the tube at the fortnight's end, the solid deposit which had gradually collected, was found to be a hydrochlorate; the alcoholic fluid was poured away and the salt washed and dried; it was soluble in hot water, and the colourless solution gave, upon gentle evaporation, a crystalline substance, in the form of opaque tufts of four-sided prisms (magnified); when dried and subjected to analysis, the crystals gave these results:

I. { 3·060 grs. dried at 212°, gave
   { 1·340 „ chloride of silver.

II. { 4·290 „ dried at 212°, gave
    { 1·895 „ chloride of silver.

	Experiment.		Calculated.		
Carbon . .			63·45	C_{34}	204
Hydrogen .			6·22	H_{20}	20
Nitrogen . .			4·35	N	14
Oxygen . .			14·94	O_6	48
Chlorine . .	10·83	10·92	11·04	Cl	35·5
			100·00		321·5

which, upon a comparison with the calculation, and the formula adjoined, which is that of morphia, will show that we have not in this case a decomposition analogous with the preceding ones; the hydrochlorate here formed is indeed the salt of morphia; its appearance and characters are identical with the latter; and the addition of ammonia to its aqueous solution, yields a crystalline precipitate, which has all the properties of pure morphia, as ascertained by various tests.

The reaction thus occurring may be explained as taking place between the chloride of amyl and the elements of water, of which morphia, as crystallized from alcohol (the state in which it was employed) retains 2 equivs. when dried in the air; indeed, they are not completely expelled, except at a temperature considerably above 212° F. So far as I remember, I used absolute alcohol; and the chloride of amyl had been, I was told, distilled from lime: at all events, when tested with nitrate of silver, it gave only slight indications of chlorine in a state precipitable by this reagent; the equation representing this change then appears to be:

$$C_{34}H_{19}NO_6, 2\,HO + C_{10}H_{11}Cl = C_{34}H_{19}NO_6, HCl + C_{10}H_{12}O_2.$$

I am not aware if the chloride of amyl has been found to undergo this transformation simply in presence of water; possibly it may, under the circumstances of my experiment; if not, the action of the morphia in this respect seems to be analogous to that of potassa, &c., in producing the alcohols from their corresponding halogen compounds.

I propose subjecting artificially dried morphia to the action of anhydrous chloride of amyl, to ascertain if the compound of this series, corresponding to the ethyl and methyl products, cannot be so obtained.

I now proceed to give the result of some experiments upon a vegetable alkaloid, closely allied in origin with the former, viz.: codeine.

ACTION OF IODIDE OF ETHYL UPON CODEINE.

About 25 grains of finely-powdered codeine were placed in a combustion-tube, about 2 feet long, sealed at one end; iodide of ethyl was poured upon it in small quantity, and absolute alcohol added in such proportion as was judged sufficient to dissolve the alkaloid; the tube was sealed. On cooling of the tube, its contents were shaken together, and a perfectly clear homogeneous fluid was obtained: the whole was placed in boiling water. In about two hours, the contents of the vessel became nearly solid, from the presence of a white, crystalline substance. This was considered to indicate the completion of the action.

Upon the appearance of the crystalline product, the tube was allowed to cool. When it was cut open, the fluid was suffered to drain off from the solid, which was then scraped out, placed upon a filter, washed with a little alcohol, and finally dried between folds of paper. The substance then presented the appearance of a highly crystalline, white mass; it was found to dissolve completely, on being covered with a small quantity of cold water. On filtering the fluid from a little dust, a tendency to crystallization was observed: this was overcome by the addition of some drops of warm water, and the clear liquid was placed in the vacuum of an air-pump, and left for a night. In the morning, although the apparent decrease in the bulk of liquid was but small, a considerable crystalline deposit was formed, which, under magnifying power, was seen to be made up of tufts of fine, silky, white needles; it was freed from the mother-liquor, and then collected and dried. An experiment on the small scale showed that the substance contained much iodine; accordingly

it was submitted to analysis. The iodine in the following analysis was determined by direct precipitation of an aqueous solution by nitrate of silver; the combustion made, of course, with chromate of lead:

5·025 grs. dried at 212°, gave
9·690 „ carbonic acid, and
2·658 „ water.
4·453 „ gave
2·300 „ iodide of silver.

	Experiment.	Calculated.		
Carbon . .	52·59	52·73	C_{40}	240
Hydrogen .	5·87	5·71	H_{26}	26
Nitrogen .		3·07	N	14
Oxygen .		10·57	O_6	48
Iodine . .	27·91	27·92	J	127·1
		100·00		455·1

These results clearly show that we have here a substance whose rational formula, as an hydriodate of a new base, may be represented thus:

$$C_{40}H_{25}NO_6, HI,$$

derived from codeine, according to the following equation, by the substitution of an atom of ethyl for an atom of hydrogen; it may be called hydriodate of ethylocodeine:

$$C_{36}H_{21}NO_6 + C_4H_5I = C_{40}H_{25}NO_6, HI = C_{36}\left\{\begin{matrix} H_{20} \\ C_4H_5 \end{matrix}\right\}NO_6, HI.$$

I immediately attempted to obtain the base by decomposition of the salt by ammonia and potash, but no precipitate was obtained even in very concentrated solutions, or on the addition of alcohol and ether. However, when the potass-fluid was boiled, it became muddy, and on cooling, an oily substance was deposited, which presented an appearance somewhat similar to codeine; but upon dissolving it in boiling water, it failed to take the crystalline character of this alkaloid under similar circumstances, for the water gave no deposit at all on cooling, and it was only by evaporation that the same oily matter again made its appearance. I am inclined to think this not the ethylocodeine, but a product of decomposition. I next attempted to isolate the base by acting on the hydriodate with oxide of silver, which was added in successive small quantities to a warm aqueous solution of the salt till it was obviously in excess; a highly alkaline

fluid was obtained, of which a small portion was evaporated to dryness at 212°; a semi-transparent, dark-coloured residue remained, which effervesced with hydrochloric acid, and dissolved to a yellow fluid, which gave, with bichloride of platinum, a yellow precipitate, at first amorphous, but becoming highly crystalline on standing; this character, as will be seen presently, belongs to the platinum-salt of ethylocodeine obtained by double decomposition, and I conclude that the new basic substance is uncrystalline, highly soluble in water, and capable of absorbing carbonic acid from the air. The nature of my materials compelled me to extreme economy, and I contented myself with this single attempt at obtaining the base itself in a dry state; its characters not being inviting for analysis any more than those of the corresponding morphia-compound, I preserved the residue of that which I had prepared, for an experiment to be described hereafter, controlling the former analysis of the hydriodate by a platinum determination in the double salt of the ethylocodeine and chloride of platinum.

The mother-liquor which had deposited the hydriodate submitted to analysis, was allowed to stand in the air; it became, after some time, again nearly filled with tufts of delicate needles, which gradually assumed a new crystalline form, the whole being transformed into well-defined, brilliant rhombic crystals of high refractive power. A portion of these was dissolved in water, and solution of nitrate of silver added; from the fluid filtered from the iodide of silver hydrochloric acid separated the excess of silver, and to the liquid again filtered was added bichloride of platinum; an amorphous precipitate immediately appeared of a pale yellow colour, but it speedily became crystalline, and on allowing the fluids to remain at rest, a salt was obtained in very fine, and well-defined, though small, rhombic crystals of a rich yellow colour; of this salt,

$$\left\{\begin{array}{l} 5{\cdot}910 \text{ grs. gave} \\ 1{\cdot}060 \text{ \,\,,\,\, platinum.} \end{array}\right.$$

The percentage calculated from this result is 17·93, which falls somewhat below that required by the formula of an anhydrous salt of ethylocodeine, which is 18·51; but as the salt was so finely crystallized, and I could perceive no obvious source of error, I am inclined to think that this base, like its parent codeine, retains an equivalent of water in this form of combination. The percentage of platinum corresponding to the formula,

$$C_{40}H_{25}NO_6,\ HCl,\ PtCl_2 + HO,$$

is here contrasted with the result of experiment,

Theory.	Experiment.
18·20	17·93

and is, I think, sufficient to prove, together with the foregoing analysis, the true composition of the base in question. When this salt is boiled in water it becomes at first resinous, then dissolves; it appears to have suffered decomposition, a substance being deposited, on cooling of the fluid, in rounded transparent granules, rather than oblique rhombic crystals.

ACTION OF IODIDE OF ETHYL ON ETHYLOCODEINE.

I mentioned that I attempted to isolate ethylocodeine by decomposition of its hydriodate by oxide of silver. A caustic fluid was obtained which, upon evaporation *in vacuo*, left an amorphous semi-transparent residue. I concluded from the experiment then mentioned with regard to a platinum-salt obtained from a similar trial on the small scale, in which the caustic fluid was evaporated to dryness at 212°, that the base so obtained was the true ethylocodeine.* It was now my object to try, by the further action of iodide of ethyl, whether the ethylation was complete, or if another atom of hydrogen could be taken away and replaced by ethyl. With this view, the residue obtained by evaporation of the alkaline fluid *in vacuo* was dissolved in absolute alcohol, iodide of ethyl added, and the whole sealed up in a tube, which was exposed to the temperature of boiling water; no crystalline deposit appearing, the action was continued for about twenty-four hours; at the end of this time the fluid became rather dark coloured, and a resinous black-looking deposit was formed. The tube was opened, the fluid poured from the deposit into a small flask, and the chief part of the iodide of ethyl distilled off; water was added to the remaining fluid, which was then placed on the water-bath and allowed to remain some hours; at the end of this time all smell of iodide of ethyl ceased, and a black substance deposited in small quantity: the fluid was filtered from this, and upon the addition of nitrate of silver, a considerable precipitate of iodide was formed; the excess of silver was removed by hydrochloric acid, and bichloride of platinum was added to the filtered fluid; an amorphous yellow precipitate was formed which, upon standing, became partially converted into a substance which, under the microscope, appeared not crystalline, but had the form of rounded grains; this was collected and analyzed. The resulting percentage of platinum obtained was 21·20, which is considerably above that of

* Possibly it had undergone slight oxidation.

codeine itself. This, and the appearance of the resinous substance—which I may mention dissolves almost completely in boiling hydrochloric acid, and is again thrown down by potash—seem to point to decomposition of quite another character than the one sought. I am unable at present to elucidate this question, but it seems worthy of investigation. It is perhaps proper to state here, that in the first experiment I made upon the action of iodide of ethyl upon codeine, the action was continued some hours after the first deposit had been observed, and that in this case also a resinous deposit was formed, the fluid was highly coloured, and the crystalline product was not nearly so well-defined in its characters. It was for this reason that the action in the experiment, the product of which gave the results stated, was stopped as soon as the large quantity of crystalline deposit appeared.

I have satisfied myself that codeine is rapidly acted upon by iodide of methyl; no doubt the resulting decomposition is similar in nature to that effected by iodide of ethyl.

The preceding experiments are not complete enough, or in some respects sufficiently decided in their results, to permit of any very definite conclusions being drawn as to the exact nature of the alkaloids to which they relate; so much, however, has been shown, I think, as to call for some attempt at deduction.

The nature of the alkaline substances produced by the action of oxide of silver upon what I have termed the hydriodates of ethylo- and methylo-morphia and codeine, would seem to ally them more closely to what Hofmann has called oxides of tetra-bases than to any other bodies. In the slight but distinct tendency they exhibit to absorb carbonic acid, they are certainly removed from any close analogy with the alkaloids from which they are derived; although, in the single analysis I have given of one of these substances, the so-called ethylo-morphia, the evident oxidation it had undergone prevents any support being afforded to this assumption on the one hand, so likewise on the other it does deprive it of any pretensions to correctness. The only conclusion I can venture to draw from the facts obtained, as to the continued action of the iodides of methyl and ethyl upon these substances, is that some change is effected which causes the formation of a basic body, having a lower atomic weight than the original compound, and the production of the resinous matters seems also to point to a breaking up of the primary molecule; but of course the experiments from which this is inferred are too incomplete to warrant any more decided opinion as to the precise

nature of the decomposition. It would follow necessarily, from the foregoing view of the constitution of the ethyl and methyl new basic compounds isolated from their salts, that if the alkaloids from which they are derived were placed in their appropriate class, according to the provisional nomenclature of Hofmann, they would come under the designation of nitrile bases; and in the decompositions in which morphia and codeine have been seen to be transformed, they would have had attached to them the elements of iodide of ethyl, for instance, as expressed thus:

$$C_{34}H_{19}NO_6 + C_4H_5I = C_{38}H_{24}NO_6, I \quad \text{and}$$
$$C_{36}H_{21}NO_6 + C_4H_5I = C_{40}H_{26}NO_6, I$$

the new salts becoming rather analogous to iodide of ammonium than to hydriodates of natural alkaloids.

Experiments made in the same direction, with others of the vegetable bases, would doubtless prove of considerable interest; since, notwithstanding both those to which I have given my attention appear to belong to the same class, as was perhaps to be expected from their being so closely allied in origin, it is extremely probable that alkaloids, contained in plants of a different natural family, will be found to possess different constitutions; I hope to examine a few.

I would venture to make one other remark before concluding this paper. The fact, that by the action of iodide of methyl upon morphia, a salt is produced, only isomeric and in no way identical with hydriodate of codeine, the base of the new salt differing so widely in character from the latter alkaloid, does not appear to me to afford great stimulus to any hopes of forming the natural alkaloids by this means; since, if we fail in the case of two natural products of the very same plant, it seems far less probable to bring about such a result as the production of a base identical with a natural formation, from a substance with which it has no relation, beyond a certain difference in their relative proportions of carbon and hydrogen.

In conclusion, I append a list of the salts I have examined, considered as iodides, in their dry and crystallized states:

Iodide of methylomorphia,	dried at 212°	$C_{36}H_{22}NO_6, I$
„ „ „	crystallized	$C_{36}H_{22}NO_6, I + 2\,HO$
„ „ ethylomorphia,	dried at 212°	$C_{38}H_{24}NO_6, I$
„ „ „	crystallized	$C_{38}H_{24}NO_6, I + HO$
„ „ ethylocodeine is	anhydrous	$C_{40}H_{26}NO_6, I$
Platinum-salt of „	dried at 212°	$C_{40}H_{26}NO_6, Cl, PtCl_2 + HO.$

XVI.—*Note on Sulphantimoniate of Copper and Zinc.*

By Professor Ettling.

(from a letter to Dr. Hofmann.)

In the January Number of the Quarterly Journal of Chemistry for 1852, p. 332, Mr. Field communicated the analysis of a new mineral which, according to the statements of Mr. Domeyko, occurs in large quantity in the Pit Altar, near Coquimbo, together with zinc-blende, iron-pyrites, and fahl-ore, and differs from the latter, especially from the zinc-fahl-ore, which is closely allied to it, by its greenish-grey colour, by giving a much lighter red streak, and by its softness.

On recalculating the results obtained by Mr. Field, who has omitted to translate his data into a formula, I find that antimony and arsenic in this ore are not present in the form of tersulphides, as in fahl-ore, but in the form of pentasulphides, as in Enargite and Xanthocon, a fact which may serve to explain the difference between the properties of this ore and zinc-fahl-ore.

Mr. Field's analysis led to the following results:

Sb.	As.	S.	Cu	Zn.	Fe	Ag.	Total.
20·28	3·91	30·35	36·72	7·26	1·23	0·07	99·82

If the amount of sulphur be calculated, which is required to convert copper, zinc, iron, and silver into sulphides, we find 13·525 per cent, leaving 16·825 per cent for the antimony and arsenic. Calculated as tersulphides, these two metals would require 10·048 per cent of sulphur, leaving an excess of 6·77 per cent. Calculated on the other hand as pentasulphides, antimony, and arsenic require 16·753 per cent leaving only the slight excess of 0·072 per cent. Hence it cannot be doubted that the new mineral is actually a *sulphantimoniate and sulpharseniate of copper and zinc.*

Since the sulphur of the basic sulphides stands to that of the acid sulphides = 13·525 : 16·753 = 4 : 5, the formula of the mineral may be written $4\,(Cu_2S, ZnS, FeS, AgS) + SbS_5, AsS_5$ or approximately $2\,(4\,Cu_2S, SbS_5) + 4\,(ZnS, FeS, AgS) + (SbS_5, AsS_5)$.

Enargite, as is well known, is $3\,Cu_2S, AsS_5$, and occurs at Morococha in Peru.

PROCEEDINGS

AT THE

MEETINGS OF THE CHEMICAL SOCIETY.

ANNIVERSARY MEETING,

March 30, 1853.

PROFESSOR DAUBENY, President, in the Chair.

The Report of the Council, and the audited Account of the Treasurer, were read (vid. p. 147).

The following gentlemen were duly elected as Council and Officers for the ensuing year:

PRESIDENT.

Colonel Philip Yorke, F.R.S.

VICE-PRESIDENTS, WHO HAVE FILLED THE OFFICE OF PRESIDENT.

W. T. Brande, M.D. Charles G. B. Daubeny, M.D., F.R.S.
Thomas Graham, F.R.S.

VICE-PRESIDENTS.

H. Bence Jones, M.D., F.R.S. Lyon Playfair, C.B., Ph.D., F.R.S.
G. D. Longstaff, M.D. Robert Warington, Esq.

SECRETARIES.

Benjamin Collins Brodie, F.R.S. Theophilus Redwood, Ph.D.

FOREIGN SECRETARY.

A. W. Hofmann, Ph.D., F.R.S.

TREASURER.

Robert Porrett, F.R.S.

OTHER MEMBERS OF THE COUNCIL.

Thomas Anderson, M.D., F.R.S.	Dr. Miller.
John Blyth, M.D.	Capt. J. W. Reynolds.
Dugald Campbell, Esq.	Thomas Taylor, Esq.
Warren de la Rue, Ph.D., F.R.S.	J. Arthur Phillips, Esq.
J. H. Gladstone, Ph.D.	George Wilson, M.D., F.R.S.
William Herapath, Esq.	A. W. Williamson, Ph.D.

The thanks of the Society were voted to the President, Vice-President, and Council, for their services during the past year.

April 4, 1853.

COLONEL PHILIP YORKE, President, in the Chair.

The following donations were announced:

"Report on the Bad Quality of Chemical Products and Drugs used by Calico Printers," by F. Crace Calvert: from the Author.

"The Journal of the Society of Arts for March:" from the Society.

"The Literary Gazette for March 19th:" from the Publishers.

"The Pharmaceutical Journal for April:" from the Editor.

A paper was read:

"On some Compounds of Urea, and on a New Method for the Determination of Chloride of Sodium and of Urea in Urine," by Baron Liebig.

April 18, 1853.

COLONEL PHILIP YORKE, President, in the Chair.

Stevenson Macadam, Esq., of Edinburgh, was admitted a Fellow of the Society.

The following donations were announced:

"The Journal of the Society of Arts for April the 8th and 15th:" from the Society.

"The Literary Gazette for April 9th and 16th:" from the Publishers.

"The Journal of the Franklin Institute for February and March, 1853:" from the Institute.

John A. Mease, Esq., of the Lake Chemical Works, South Shields, was elected a Fellow of the Society.

The following papers were read:

"On the general distribution of iodine and bromine:" by Stevenson Macadam.

"On the solid compound obtained by distilling stearic acid with lime:" by Thos. H. Rowney Ph.D.

May 2, 1853.

COLONEL PHILIP YORKE, President, in the Chair.

The following donations were announced:

"The Literary Gazette," 3 Numbers: from the Publishers.

"The Journal of the Society of Arts," 2 Numbers: from the Society.

"The Pharmaceutical Journal," for May: from the Editor.

Becquerel, M., "Traité Experimental de l'Electricité et du Magnétisme et de leurs Rapports avec les Phenomènes naturels," Tomes VII, 8vo, Paris, 1834-40.

Bergman, "Physical and Chemical Essays," by Edmund Cullen, M.D., 8vo, London, Vol. III, 1788-91.

Berzelius, J. J., "Traité de Chimie," traduit par A. J. L. Jourdan, Tomes VIII, 8vo, 1829-33.

Chaptal, M. J. A., "Elements of Chemistry," translated from the French, Vol. III, 8vo., London, 1800.

Cramer, John Andrew, M.D., "Elements of the Art of Assaying Metals," in 2 Parts, 8vo., London, 1741.

Fritschius, John Christian, "The Principles of Pyrotechnical Metallurgy and Metallick Essaying," 12mo.

Gellert, C. C., "Metallurgic Chemistry," 8vo., London, 1776.

Girtanner, Christoph, "Anfangsgründe der Antiphlogistichen Chemie," 8vo., Berlin, 1795.

Glauber, John Rudolph, "A description of New Philosophical Furnaces, or a New Art of Distilling, also a description of the Tincture of Gold, or the true Aurum Potabile," 12mo., London, 1651.

Greu, Dr. Friedrich Albrecht Carl, "Grundriss der Chemie," Erster Theil, 8vo., Halle, 1796.

————, "Systematisches Handbuch der gesammten Chemie," 8vo., Band II, Erster Theil, 1795.

"Pyritologia, or a History of the Pyrites," translated from the German, by J. H. Henckel, 1757, 8vo., London.

Henry, Wm., M.D., F.R.S., "Elements of Experimental Chemistry," Vol. II, 8vo., London, 1826.

Klaproth, Martin Henry, "Analytical Essays towards the Promoting the Knowledge of Mineral Substances," 8vo. London, 1801.

Lagrange, J. B. Bouillon, "Manual of a Course of Chemistry," Vol. II, 8vo., London, 1800.

"Metals, Mines, and Minerals—A Collection of scarce and valuable Treatises upon." In four Parts, 12mo., London, 1738.

Webster, John, "Metallographa; or, an History of Metals," 8vo., London, 1671.

Packe, Chr., "153 Chemical Aphorisms," 32mo., London, 1688.

Sandivogius, Michael, "A New Light of Alchemy taken out of the Fountain of Nature and Manual of Experience," to which is added "A Treatise on Sulphur," "Nine Books on the Nature of Things," also, "A Chemical Dictionary, explaining hard places and words met withal in the writings of Paracelsus, and other obscure authors."

Valentine, Basil, "Chariot of Antimony," with Annotations of Theodore Kirkringius, M.D., 12mo., London, 1678.

From Henry James Brooke, Esq., of Clapham Rise.

A communication was made:

"On Deposits of Soluble or Gelatinous Silica in the Lower Beds of the Chalk Formation:" by John Thomas Way.

May 16, 1853.

PROFESSOR GRAHAM, Vice-President, in the Chair.

The following donations were announced:

"The Quarterly Journal of the Geological Society:" from the Geological Society.

"The Literary Gazette," 3 numbers: from the Publishers.

"The Journal of the Society of Arts," 2 numbers: from the Society of Arts.

The following papers were read:

1. "On a Compound Sulphate of Potash and Soda:" by J. H. Gladstone, Ph.D.
2. "Note on Thierschite:" by J. Liebig.
3. "On Kyanurenic Acid:" by J. Liebig.

June 6, 1853.

PROFESSOR GRAHAM, Vice-President, in the Chair.

The following donations were announced:

"Bulletin de la Classe Physico-mathématique de l'Académie Impériale des Sciences de St. Petersbourg," Tom. IX and X: from the Academy.

"The American Journal of Science and Arts," for May, 1853: from the Editors.

"On the Relations between the Atomic Weights of Analogous Elements:" by G. H. Gladstone, Ph.D.: from the Author.

"Literary Gazette," 3 numbers: from the Publishers.

The following papers were read:

1. "Analysis of the Waters from the Deep Well of the Westbourne Water-works at Westbourne Grove, of the Well in Russell Square, and the Artesian Well at the Hanwell Asylum:" by Charles Harwood Clarke, M.A., F.S.A., and Henry Medlock, F.C.S.

2. "On the Increase in Weight of Molasses Casks, occasionally arising from Absorption:" by William Ferguson.

3. "On some New Basic Products obtained by the decomposition of Vegetable Alkaloids:" by Henry How.

June 20, 1853.

Colonel Philip Yorke, President, in the Chair.

Andrew Tomlin, Esq., of Valparaiso, was elected a Fellow of this Society.

The following communications were made:

1. "On the Conditioning of Silk:" by P. J. Chabot, M.A.

2. "On a New Method of Estimating the Strength of Chloride of Lime:" by Dr. Astley P. Price.

3. "On a Gas-furnace for Organic Analysis:" by Dr. Hofmann.

ANNUAL GENERAL MEETING,

MARCH 30, 1853.

REPORT OF THE COUNCIL.

The Council in presenting the following returns from the Secretaries and Treasurer, are again able to announce that the state of the Chemical Society continues satisfactory, both as to its present condition and future prospects.

STATEMENT OF THE NUMBER OF FELLOWS OF THE CHEMICAL SOCIETY AT THE PRESENT TIME, AND AT THE CORRESPONDING PERIOD OF LAST YEAR.

Present number of Fellows		241
Deaths, resignations, &c., since last Anniversary Meeting	20	
Elected since last Anniversary Meeting	16	
Decrease since last Anniversary Meeting		4
Number of Fellows at period of last Anniversary Meeting .		245

In reference to the small diminution in the number of Fellows, it is right to mention that the names of thirteen Fellows, who had for some time ceased to pay their subscriptions, have, since the last Report, been removed by the Society from the list, in compliance with Bye-law IV.

FELLOWS DECEASED.

John Sylvester, Esq., 96, Great Russell Street.

Thomas Thomson, M.D., F.R.S. L. and E., F.G.S., &c., Glasgow.

AUDITED REPORT OF THE TREASURER.

Dr. ROBERT PORRETT (TREASURER) IN ACCOUNT WITH THE CHEMICAL SOCIETY. *Cr.*

1852.		£.	s.	d.	1853.		£.	s.	d.
March 30.	To Balance from last Account	91	12	2	March 26.	By payment to Directors of Polytechnic Institution, for One Year's Rent of Rooms to 25th inst.	120	0	0
1853.									
March 26.	„ Subscriptions (£327) and Compositions (£60) since received	387	0	0	„ „	„ Ditto to Henry Watts, for One Year's Salary as Editor of the Society's Journal . . .	50	0	0
„ „	„ Admission Fees from 22 new Members . .	44	0	0	„ „	„ Ditto to H. Baillière, for Publishing the Society's Journal	103	2	6
„ „	„ One Year's Dividend on £300, 3 ℔ Consols, minus Property Tax	8	14	10	„ „	„ Ditto to John Kirkman, for Attendance and for Tea, Coffee, &c.	40	6	4½
„ „	„ One Year's Rent in advance, to January, 1854, from the Meteorological Society, for use of Rooms	20	0	0	„ „	„ Ditto to J. Bonomi, for Model of Common Seal	5	0	0
„ „	„ Proceeds of Sale of "Memoirs" . . .	3	12	4	„ „	„ Ditto to G. Barclay, for Common Seal and Press	29	0	0
					„ „	„ Ditto to C. Whiting, for Printing . . .	11	10	6
					„ „	„ Ditto for Books, Stationery, Postage-stamps, &c.	24	8	3
					„ „	„ Ditto to the Collector, for his Poundage .	15	19	0
					„ „	„ Ditto to Imperial Gas-Light Company . .	1	13	3
					„ „	„ Ditto for Ironmongery and Gas-Fittings .	6	2	5
					„ „	„ Ditto to Robert Ireland, for Book-cases .	11	18	0
					„ „	„ Ditto for Chemicals	2	14	0
					„ „	„ Ditto to Hannell & Ellis, for a Glass-case .	9	0	0
					„ „	„ Ditto to J. Giller, for Plate-glass to a Case .	0	12	0
					„ „	„ Ditto to National Linen Company, for Damask	0	14	6
					„ „	„ Balance carried to next Account . . .	122	18	6½
		£ 554	19	4			£ 554	19	4

London, March 26, 1853,

R. PORRETT, Treasurer.

Examined and found correct,

(Signed) { ALFRED SMEE, JOHN J. GRIFFIN, CHARLES HEISCH, } Auditors.

LIST OF PAPERS READ AT THE CHEMICAL SOCIETY SINCE THE LAST ANNIVERSARY MEETING.

"On the detection and qualitative separation of Tin, Antimony, and Arsenic; and on the relation existing between these metals and others which are precipitated from their acid solutions by Sulphuretted Hydrogen." By Charles L. Bloxam.

"Researches on the Constitution of Organic Acids." By M. Charles Gerhardt.

"Note on the preparation of Carbonate of Amyl." By John A. Bruce.

"New formation of Salicylic Acid." By Dr. Gerland.

"On the preparation of Anhydrous Acetic Acid." By M. Charles Gerhardt.

"Chemical Memoranda." By Robert Warington.

"On the action of Ammonia upon Binoxysulphocarbonate of Amyl." By Matthew W. Johnson.

"On a New Process for the detection of Fluorine when accompanied with Silica." By George Wilson, M.D.

"On a New Test for Strychnia." By Mr. J. H. Pepper.

"A Note on the existence of Strontia in the Well-waters of Bristol." By Messrs. William and Thornton J. Herapath.

"On a new method for the Analysis of Chrome Ores, and on Commercial Chlorochromate of Soda." By F. Crace Calvert.

"On certain Isomeric Transformations of Fats." By Patrick Duffy.

"On the qualitative separation of Arsenic, Tin, and Antimony." By Geo. F. Ansell.

"Observations upon a new series of Double Chlorides containing Diplatosammonium." By G. B. Buckton.

"On the action of Iodine on Phosphorus." By B. C. Brodie.

"On the Acid Oxalates of the Earths." By Edward Clapton.

"Researches on the Anhydrous Organic Acids." By Charles Gerhardt.

"On the valuation of Indigo." By Dr. Frederick Penny.

"Note on the Presence of Alumina in the Urine." By Lionel S. Beale.

"On the reaction of Glycocoll with Potash." By Professor Horsford.

"On the constitution of Stearine." By Patrick Duffy.

"On the Compounds of several essential Oils with the Alkaline Bisulphites. By C. Bertagnini.

"On some New Compounds of Tellur-ethyl." By Professor Wöhler.

"Analytical Notes." By A. B. Northcote and A. H. Church.

"On the Law of Electrolysis." By Professor H. Buff.

"On the mode of estimating the value of Red Prussiate of Potass, and of testing the strength of Bleaching Liquors." By Francis Lieshing.

ANNIVERSARY ADDRESS OF THE PRESIDENT.

CHARLES DAUBENY, M.D., F.R.S., &c.

GENTLEMEN,

At our last Anniversary Meeting, I took occasion to descant upon the advantages that might accrue to science from the juxta-position of the different chartered Societies devoted to this object, in some convenient and central locality.

You may recollect my having then stated, "that I for one should heartily hail the day, which might witness the assemblage of all the principal Bodies dedicated in this place to the study of Nature under one and the same roof, pursuing their separate labours indeed independently, but at the same time deriving mutual support and assistance from their contiguity; exercising over each other no paramount jurisdiction, but moving onwards in harmony and concert, as became the federal members of the great Republic of Science."

My opinions with regard to the desirableness of such an arrangement have since that period by no means undergone a change; nor am I aware that, in expressing the above sentiments on the occasion referred to, I said anything in which the great body of the Society over which I presided would not, at the time, have heartily concurred. Nevertheless, since we last met, circumstances have transpired with respect to the views of Government, in relation to the mode of carrying out the object alluded to, to which I confess myself as little able to assent, as any other of our Members can be.

It appeared from certain remarks which fell from the late

Chancellor of the Exchequer, in a speech delivered by him in the course of the preceding session, that it was then in the contemplation of Government to purchase a piece of land at Kensington Gore, partly under the expectation, that the chartered Scientific Societies of the Metropolis would accept as a boon the offer of any suitable suite of apartments which might be there erected at the public expense, as being a mode of realising a project, in which, it was presumed, that they all entertained a common interest.

Now, as a general repugnance was felt throughout the Societies referred to, to a removal to so distant a locality, it seemed necessary, that whilst we expressed, as in duty bound, our acknowledgments for the liberal disposition towards Science evinced by her Majesty's Government, we should at the same time, one and all, in order to prevent misapprehension, intimate our dissent to the particular scheme, by which our interests were thought to be consulted. And with regard to this Society in particular, I am persuaded, that the difficulty which most of our Members would find in resorting to so remote a part of the suburbs, for the purpose of attending our Meetings, would greatly counterbalance any advantage that might accrue from the gratuitous supply of apartments, even if by so doing we could hope to bring about that general juxta-position of scientific bodies, which we are all agreed to consider as desirable.

But it could not be forgotten, that three at least of the Societies included in this proposed arrangement are already provided with gratuitous accommodations in a central part of London, and are therefore less likely, even than ourselves, to consent to a removal to a more distant locality.

Without, therefore, presuming to anticipate what may be deemed convenient or advantageous hereafter, when perhaps the tide of population may roll westward, and the facilities of communication between distant parts of the metropolis may be increased, the Council deemed that they were not stepping beyond their proper functions, in protesting at the present time against the contemplated removal; and with this intent, directed me, as their President, to state to the Royal Society, in reply to a minute of the Council of that Body, having reference to this proposition, "that whilst they are ready to aid in promoting a practicable scheme, for the juxta-position of the said Scientific Societies, they are decidedly of opinion, that a removal of their library and place of meeting to Kensington would be seriously detrimental to the interests of the Chemical Society."

It will give me sincere pleasure to find, either that this or some future Government may be sufficiently alive to the importance of

Physical Science, and sensible of the disadvantages under which it struggles in this country through the dispersed state of the Societies formed for its cultivation, to provide us all with some central and convenient establishment, where we can pursue our labours in common; but until this day arrives, let us be encouraged by recollecting what our predecessors in the same field have accomplished without such extraneous aid, and what it may be possible, therefore, for us also to achieve by our own unassisted efforts.

Of this, indeed, the illustrious chemist who has been lost to us since our last Anniversary—I mean Dr. Thomas Thomson of Glasgow—affords us, as I conceive, one of the most instructive examples.

In early youth, not only without any of those appliances which some chemists, at least in foreign lands, have derived from their respective governments, but even without any further scientific training than what he could obtain from the public courses of lectures delivered at Edinburgh; in spite, too, of restricted means, and the absence of private patronage, he gradually raised for himself a reputation for extensive knowledge, which placed him in the first rank amongst the cultivators of his own particular Science. Indeed if amongst the chemists of the last generation, Dr. Dalton stood pre-eminent for the comprehensiveness of his generalisations, and Sir Humphry Davy for the brilliancy of his discoveries, Dr. Thomson may be regarded as holding the foremost place for his acquaintance with the facts of the Science, his careful digest of all that was then known in its several branches, and his impartiality in assigning to each contributor his appropriate share of merit.

At a time when no Treatise on Chemistry worthy of the name existed in Great Britain—when the greater part of what had been known in this country was obtained through the medium of translations from foreign languages, and when the facts recorded were put before us, often without much attempt at method or logical precision—Dr. Thomson surprised the world at an early age, by the publication of a System, in which the substances that came under his review were classified and arranged in such a manner, as to denote their mutual relations, and to exhibit the due subordination of their properties one to the other.

It may be doubted indeed, whether for the purposes of study, the analytical method of imparting knowledge, which he preferred adopting, is the one most advisable; it would rather seem, that instead of following, as he has done in his Treatise, the order of discovery, it might be better to commence with a statement of the general principles of the Science, and afterwards to enter in detail

upon the properties of the individual substances, whose phenomena have guided our predecessors to the general laws applicable to them all.

But admitting this as a defect in Dr. Thomson's arrangement, the clear and exact manner in which he reduced to order the facts scattered at the time he wrote over a thousand different publications, demands from us our warmest acknowledgments.

It may be difficult, indeed, to say, whether Dalton would have been able to establish the existence of those definite combinations between bodies upon which his Atomic Theory was mainly built, but for the laborious and accurate statements which Dr. Thomson had brought together in his Treatise, with respect to the composition of various salts. Nor ought it to be forgotten, that at the early period, when Wollaston received with hesitation, and Davy with ridicule, the theory which the penetration of Dr. Dalton had first pointed out, Thomson stood forward as its warmest advocate, and supported it with some of the most convincing of its proofs.

Nor were his services in diffusing knowledge confined to the accurate record of facts contained in his System of Chemistry. For nine years—namely from 1813 to 1822—he conducted the "Annals of Philosophy," a Periodical in which he did not content himself with a mere publication of Essays on scientific subjects, communicated to him by others, or to a bare report of any new discoveries made in this or in other countries, but also introduced each year a Digest of the progress of Science in its various departments, in which the merits of each contributor were discussed with freedom, but always with perfect frankness, and with an entire absence of prejudice and party feeling.

In this undertaking, no less than in the first introduction of that system of symbolic writing which is now in common use amongst chemists, Dr. Thomson may be said to have pointed out two most efficient instruments for the advancement of his favourite Science.

The former proved the prelude to those comprehensive Reviews of the annual progress of Chemistry, which were for many years given to the world by Berzelius; the latter, after having been extended and improved by the distinguished Swede, found at length a general reception in the country in which it originated.

At a later period of his life, he published his "Attempt to establish the first Principles of Chemistry by Experiment," a work which was censured by Berzelius, with a severity stimulated, no doubt, by the opposition between the results therein arrived at, and his own; although there may be some ground for alleging, that our con-

fidence in his accuracy is impaired by doubts as to the correctness of the data upon which he proceeded.

The work, however, must be allowed by all unprejudiced persons to exhibit marks of the most persevering industry, and to supply us with much valuable information.

For a candid review of its merits, I may refer you to Mr. Crum's excellent Sketch of the Life and Labours of Dr. Thomson, in which the author, without disguising the defects imputed to the treatise in question, or seeking to extenuate unduly certain errors which attach to the principle upon which the calculations in it are founded, successfully vindicates his former master from the charge of dishonesty, or at least of wilful carelessness in the conduct of his experiments, which had been most unfairly brought against him.

Whilst, however, I willingly leave this part of the subject in abler hands than my own, I cannot refrain from adding, that his adoption, in the work in question, of Dr. Prout's ingenious suggestion, that all other bodies were multiples of hydrogen, seems at length, notwithstanding the adverse verdict of the great Swedish chemist alluded to, and of others respecting it, borne out with regard to oxygen, carbon azote, and calcium, by the elaborate researches of Dumas and Marignac, whilst other experimentalists appear to have since successfully reduced sulphur, zinc, silver, mercury, and iron to the same standard.

And when we recollect, on the one hand, how numerous are the sources of error which may creep into the best devised series of experiments, and, on the other, how infinite are the chances against our arriving, by any erroneous and therefore fortuitous results, at numbers which turn out to be exact multiples of the atomic weight of hydrogen, the argument in favour of Prout's doctrine, founded upon the coincidence of the figures in the cases above cited, seems greatly to exceed in strength that which can be alleged against it, from the non-accordance between experiment and calculation in the instance of a few other elementary bodies.

As an Historian of Science also, Dr. Thomson's merits were of a high order, from his candour, frankness in expressing his opinion, and diligence in ascertaining facts; indeed, his biographical notices supply us with some of the most valuable records we possess, with respect to the lives and characters of Chemists in this and the last century.

As Professor of Chemistry at Glasgow, an appointment which he held from the year 1818 till the period of his death in the summer of last year, Dr. Thomson had the satisfaction of training many who

have done honour to the school which he instituted, either by their scientific, or their practical contributions to Chemistry. Need I mention the names of Graham, of Walter Crum, Hugh Colquhoun, Alexander Harvey, Johnston of Durham, of Clark, and of Stenhouse, as exemplifications of this fact; or remind you that my only motive for passing so lightly over this portion of Dr. Thomson's services is the fear of offending the modesty of some of his surviving pupils who may chance to be present ?

I cannot, however, terminate these remarks, without observing, that the career of Dr. Thomson affords to the young chemist a cheering proof of the advances that may be made in Science, even under great original disadvantages, by an understanding, solid rather than brilliant, and marked more by sagacity and common sense than by genius and originality ; provided only these powers of mind are, as his were, concentrated through life upon certain special objects, and are stimulated into exertion by no more selfish and ignoble principle than the pure love of scientific truth.

We have also lost since our last Anniversary, Mr. John Sylvester, a gentleman eminent for his successful applications of the Science of Engineering to domestic purposes. He was the son of Mr. Charles Sylvester, the well-known author of the "Philosophy of Domestic Economy," the principles of which he applied with so much sagacity in the case of the Derby Infirmary, as thereby to establish his reputation as a civil engineer. It was no doubt in great measure to the attentive study of his father's theory and practice, that we may attribute the expertness which our late Fellow displayed in the execution of large works for warming and ventilating buildings, as well as the success which attended some of his inventions, as in the case of the Radiating Stove Grate, now in such general use.

Mr. Sylvester was particularly happy in his contrivances for warming the Arctic Discovery ships, sent out under Captains Parry, Ross, and others; and it is said that the Ridge and Furrow Roof, so successfully applied by Sir Joseph Paxton to the Crystal Palace, had been previously adopted by Mr. Sylvester in the forcing houses he constructed for Mr. Strutt of Derby, in the year 1844. He was also an accomplished amateur-draughtsman, and was much regretted by his personal friends for his many amiable qualities.

His decease in the August of last year was occasioned by an obscure complaint, from which he had for a considerable time been a sufferer.

In vacating the Chair, which I have had the honour to occupy during the last two years, I am happy to think I am leaving the Society in a satisfactory state, both as regards its present condition and its future prospects.

We have, indeed, at two or three of our Meetings been left without a supply of matter, an accident more likely to occur in a Chemical Society than in one of a more miscellaneous and discursive character; and, indeed, when we reflect how many bodies, medical, pharmaceutical, and agricultural, divide with us the fruits of the labours which are carried on by chemists, not to speak of the number of chemical papers, which, as I remarked in my last Address, are communicated by us to the Royal Society, and appear in its Transactions, we need not be surprised if the supply of matter has not always kept pace with the activity of our Members, or with the interest which the Science is exciting in the mind of the public.

The flow of original communications has indeed of late been somewhat of an intermittent character, sometimes copious, sometimes deficient; but it is but fair to add, that whenever a void has occurred at our Meetings, it has been so well filled up by discussions of a general scientific interest, as to leave to those who attended little reason to regret that no new series of researches had been submitted to them on those occasions.

Our Members, however, ought not to forget, that this Society has the first claim to the services and contributions of those enrolled in it; and that, even if the researches they are carrying on seem of that practical or technical character as to demand, in the first instance, a different destination, it may be for the mutual advantage of themselves and of the Society that they should be subsequently submitted to us, as the merits of the scientific principles they involve are nowhere likely to be so satisfactorily or so fully canvassed as at the Meetings held in this room.

It is, moreover, a subject of regret to me, that nothing should have been done during my Presidentship, either by myself or others, towards simplifying and methodising the existing nomenclature of organic substances, which at the present time seems to proceed upon no fixed basis, or, at least, is guided by such rules only as may exist floating in the minds of the leading chemists who have most advanced this part of their Science, and which have never yet been distinctly enunciated. In a communication made to the chemical lecturer of the British Association at Ipswich, two years ago, I took occasion to point out what those rules apparently were, so far as

could be gathered from the practice of the individuals alluded to; and by so doing, may perhaps flatter myself with having contributed somewhat, towards promoting that uniformity and consistency in the use of the terms selected for designating newly-discovered compounds, which is in many respects so desirable.

But the larger and more ambitious scheme which I had once contemplated—that of enlisting the leading chemists of the country, and of this Society in particular, in the attempt to frame a general system of nomenclature, which might embrace the whole of Organic Chemistry—I have been induced to postpone, from considering the unsettled state of certain fundamental questions, upon which so much of the terminology as well as of the notation of organic bodies is necessarily dependant.

The Society is watching with interest the development of those views, which have more than once been brought before our notice, "On the condition of Elements at the moment of Chemical Change," views, which, if adopted, would tend to modify many of our ideas with respect to chemical or electric affinity; tending, as they do, to the conclusion, that the particles of an elementary body are held together, not by that force which we term cohesive attraction, but by a kind of chemical affinity brought about in them, as it is in the case of compound bodies, by certain differences in the electrical condition subsisting between their particles.

The ingenious speculations also of another of our colleagues, by the aid of which he explains in so novel a manner the theory of etherification, appear to be based upon a similar principle, inasmuch as, instead of that fixity which was supposed to be involved in the very idea of a stable and definite compound, they assume a constant movement amongst its particles, arising, as it should seem, from some difference in their electrical condition.

To such a view, indeed, I am myself the more reconciled, as it is quite in harmony with the speculations which I ventured to indulge in at the time of the publication of the last edition of my Atomic Theory.*

I then remarked, that "if the particles, into which heat is capable of resolving matter, when it assumes the gaseous condition, be themselves divisible into still minuter ones under the influence of chemical affinity; and if even the latter, perhaps, are composed of groups of atoms, rather than of single ones, it is conceivable that every one of these groups, within its own little world, should admit of such an

* Introduction to the Atomic Theory, p. 278.

alteration in the position of its respective particles, as may serve to affect the properties it possesses, and consequently its relations to other bodies; although no one of these particles can separate itself from the group, of which it constitutes a part."

This intestine movement amongst the particles of a solid body seems likewise confirmed by the phenomenon of *allotropism*, and by the change of form, colour, &c., which occurs in many bodies after crystallization; whilst on a larger scale, the same is attested by many circumstances remarked by geologists with regard to the formation of mineral veins; the segregation of certain substances from the general mass of the containing rock; and other molecular changes which appear to be taking place within the bowels of the earth.

And since this mobility of particles is extended even to those which constitute the mass of a solid body, the theories of chemists in this respect seem tending to the same point as those of geologists, inasmuch as the former suppose a continual oscillation in the molecules of a body, owing to the interchange which is taking place between them; whilst the cosmogonists of the present day maintain the same with respect to the solid fabric of the globe, which their predecessors figured to themselves as the very emblem of stability.

The theory, however, which in the case before us is built upon this postulate, requires for its adoption such a revulsion in our ideas with respect to the relations between ether and alcohol, as would involve in the end a new nomenclature, as well as a fresh method of notation. We should be called upon to alter the atomic weights of all the other elements, by doubling the number of atoms of hydrogen assumed to be present in water; and instead of regarding ether simply as the oxide of an hydrocarbon, and alcohol as its hydrate, we should have to figure to ourselves the former as produced from water, by the replacement of one of its hydrogen atoms, and alcohol by that of both.

Such a view of the composition of these and other allied bodies has, indeed, much to recommend it, and deserves, in my humble opinion, the attentive consideration of chemists; but it is one thing to receive a new theory with favour, and to entertain it with attention; and another to admit it so entirely into the category of established truths, as to mould all our other views in accordance with its principles.

In framing a system of chemical nomenclature, therefore, at the present moment, we should neither be justified in ignoring the existence of theories which have already taken a certain hold upon the minds of eminent chemists, both in this and in other countries; nor

could we venture to propose them as the basis of our scheme, whilst still under discussion, and perhaps but imperfectly developed as yet even in the minds of the individuals who have promulgated them.

To discuss however, as they deserve, these and other theoretical views, which occupy so prominent a place in the Journal of our Society, would be impossible, without transgressing the limits which custom has hitherto assigned to your President's Anniversary Addresses.

Here, therefore, I might be inclined to pause: but lest it should be imagined that our Members are exclusively absorbed in the speculative departments of Chemistry, to the neglect of the practical, I will briefly allude to the important services rendered to the cause of agriculture by Professor Way, in the course of the various researches he has been carrying on in behalf of the Royal Agricultural Society; and especially by the manner in which he has elucidated the problem relating to the absorbent power possessed by different soils with reference to manures, and in which he has traced to its principles the property which belongs to Clay, of arresting in their downward progress the organic matters present in the water which percolates the earth, and even of separating from this solvent its most valuable saline contents—namely, the ammoniacal and other alkaline constituents with which it may be impregnated. And this, too, he has shown to be done by means of a double decomposition carried on in apparent contravention of the received laws of elective attraction. A discovery of this kind is not less important from its practical applications, than it is interesting in its bearings on the general principles of the Science; and although not announced in the pages of our Transactions, deserves to be mentioned as the fruit of the persevering researches of a chemist, who is enrolled in the list of our Fellows.

Nor will it, I hope, be deemed irrelevant for me to allude to the important application of Scientific Chemistry to the solution of certain Geological Problems, which has been carried out by one of the most distinguished of our Foreign Members.

Those who have taken the trouble of perusing my work on Volcanos, and especially the second edition of it, published in 1848, will recollect, that in bringing forward that theory which may be regarded as a revival, or perhaps a development, of the original hypothesis of Sir Humphry Davy, my professed object principally was that of enlisting the services of chemists in an attempt to elucidate a series of phenomena, which, although essentially chemical, had been hitherto, in a great degree, abandoned to geologists.

Indeed, since the time when Gay-Lussac published his "Remarks on Vesuvius," and that at which Sir Humphry Davy paid a cursory visit to the same spot, no chemist of European reputation appears to have made volcanos a subject of study; excepting Abich, to whom we owe the first lucid sketch of the chemical relations which volcanic and plutonic rocks bear to each other; and Professor Bischoff of Bonn, whose researches were, however, confined to extinct volcanos, such as those of the Rhine and Eyfel.

Hence it is not to be wondered at, that the subject should be treated as though it were exclusively a mechanical problem, and theorised upon without any due appreciation of the interesting chemical phenomena which it presents to our notice.

It was this consideration more especially which led me, in my work on Volcanos, to give a prominence to those points which appeared to have been unduly neglected by others; and to advocate with more zeal than I might otherwise perhaps have felt inclined to do, a theory, which necessarily brought before us the nature of the gaseous, saline, and crystalline products, which proceed from the internal focus of its action.

That this was my object, will appear from some remarks which I made fifteen years ago, in my "Report on Mineral and Thermal Waters," undertaken at the request of the British Association for the Advancement of Science, and published in their Transactions.

"We ought," I observed "carefully to distinguish between that which appears to be a direct inference from observed fact, and what can at most advance no higher claim than that of being a plausible conjecture. The general occurrence of volcanos in the neighbourhood of the sea, and the constant disengagement of aqueous vapour, and of sea-salt from their interior, are facts that establish in my mind a conviction that water finds its way to the seat of the aqueous operations, almost as complete, as if I were myself an eye-witness of another Phlegethon, discharging itself into the bowels of the earth, in every volcanic district, as in the solitary case of Cephalonia."

"Nor is the access of atmospheric air more questionable than that of water; so that the appearance of hydrogen united with sulphur, and of nitrogen either alone or combined with hydrogen at the mouth of the volcano, seems a direct proof, that oxygen has been abstracted by some process or other from both."

"Having satisfied our minds with regard to the fact of internal oxidation, we naturally turn to consider what principles can have existed in the interior of the earth capable of abstracting oxygen from water, as well as from air; and this leads us to speculate on the basis of

the earths and alkalies, as having been instrumental in causing it. But in ascribing the phenomena to the oxidation of these bodies, we ought not to lose sight of the Baconian maxim, that in every well-established theory, the cause assigned should be not only competent to explain the facts, but also *known to have a real existence*, which latter circumstance cannot, of course, be affirmed of the alkaline and earthy metalloids, as having a place in the interior of the earth."

I should not despair of being able to show that such an hypothesis is still tenable; but it will be more profitable on the present occasion, as well as, I doubt not, more agreeable to my hearers, for me to point out the substantial additions which Professor Bunsen has supplied to our knowledge of this class of phenomena.

He has, in the first place, proved that the products of volcanic action—at least as they display themselves in that vast *focus* of internal energy which we observe in the Island of Iceland—consist only of two kinds of material: either a trachytic rock, consisting of a trisilicate of alumina, conjoined with a similar compound of silica with an alkali or alkaline earth; or else an augite rock, in which 1 atom only of silica is combined with 2 atoms either of alumina, protoxide of iron, lime, magnesia, potass, or soda.

Bunsen has given a formula, by which the proportion between these two constituents, in any given rock, may be readily computed; and hence concludes, that the products of volcanic action in Iceland are derived from *two* independent *foci*.

But the most interesting part of his researches relates to the changes which have been wrought upon these materials by causes of subsequent operation.

Few of the friends I see around me on the present occasion are old enough to have witnessed the contests which for many years were waged with so much fury between the advocates of the igneous and aqueous origin of basalt.

In this controversy much stress, I recollect, was laid by the Wernerians on the characters of trap-tuff, which, it was contended, could by no means admit of being referred to the action of heat, whilst its passage into trap-rocks rendered it difficult to ascribe to the one an origin which was denied to the other.

Now, Professor Bunsen has, in the first place, beautifully shown that the species of tuff, which prevails in Iceland, and which is also abundant in Sicily, as is implied by its name *Palagonite*, derived from the village of Palagonia at the base of Etna, possesses such a chemical composition as identifies it with the pyroxenic rock of the neighbourhood.

He has also succeeded in explaining those differences in structure and in appearance, which, in spite of this correspondence in the nature of its constituents, stamp it as a distinct mineral; having traced such alterations to the operation, not indeed of water alone, but of an alkali, or an alkaline earth, containing just so much water as to exist in the condition of a hydrate, formed in either case by the influence of a temperature equal to that of ignition.

The Professor states, that he has actually succeeded in converting basalt into palagonitic tuff, by mixing it in a state of fine powder with 13 times its weight of slaked lime, or of potass.

Thus, the very alkali, which may have been sublimed from some internal *focus* of igneous action, might, if water were also present, have been instrumental in converting an ordinary pyroxenic rock into palagonite under the influence of heat.

Another difficulty which besets the Huttonian theory, arose from the existence of zeolites in the midst of rocks of supposed igneous formation; as the readiness with which these minerals part with their water, seemed inconsistent with the supposition of their originating at a high temperature.

This was got over by supposing such minerals to have been formed under a pressure sufficient to prevent the water from escaping, and hence the Vulcanists were in some cases driven to assume pressure, where none could be shown to have existed.

But Bunsen has relieved them from this embarrassment, by demonstrating, that zeolites may be generated, by fusing lime and silica with an excess of caustic potass, without any pressure at all: and that by this method crystals may be produced at a red heat containing water, of which, however, the greater part is disengaged at a temperature not exceeding 228°, when the substance is detached from the crucible in which it had been formed.

Professor Bunsen has also, by a series of decisive experiments, removed all doubts as to the nature of the aeriform bodies which are disengaged from volcanos, and has fully substantiated, what my own observations, and those which I had collected from various other sources, led me to infer—namely, that inflammable gases, made up, either wholly, or in part of hydrogen, are amongst the most constant concomitants of volcanic action in all its various phases. Nitrogen also, often unaccompanied with oxygen, seems to be as common in the fumaroles of Iceland, as I have found it to be in the thermal springs of other volcanic regions.

And with respect to the origin of these gases, Bunsen most satisfactorily refutes the idea of his countryman Bischoff, who refers them to the spontaneous decomposition, or dry distillation of organic

matters, showing that when this process takes place, nitrogen is invariably accompanied with marsh gas and other hydrocarbons which are never present in volcanos.

He accordingly expresses his decided opinion, that the objections which have been supposed to be fatal to the old volcanic theory of Davy, entirely lose their value after these results. "For if," he remarks, "in the spirit of this theory, it is assumed, that the lavas, and the phenomena of ignition accompanying them, result from an oxidation of alkaline and earthy metals, determined by a decomposition of water, it admits of being proved, that the quantity of the hydrogen evolved from volcanos, bears a perfect relation to the magnitude of the streams of lava formed."

A single one of the vapour springs of Krisuvik yields, according to Bunsen's own calculations, about 12 cubic metres of hydrogen in 24 hours.

"Assuming, then, that the remaining innumerable springs, together with the large fumaroles occurring there, yield together a quantity only 100 times as great—which may safely be regarded as far less than the quantity of this gas which is actually evolved—we may, by means of this assumption and simple calculation, show, that the formation of lava, which would be equivalent to such an evolution of gas within the period which elapses between two great eruptions, is sufficient to produce immense streams of lava."

"Nor is it any longer possible to attach importance to the second of the principal objections which have been made to Davy's hypothesis—namely, that it is unusual to observe any sensible appearance of flames during great volcanic eruptions. For if, from the known composition of the first-mentioned fumarole gas, we estimate the temperature of its flame, we find it to be $305^{0}{\cdot}6$; consequently, a temperature which is far below the point of ignition of hydrogen. These gases are, therefore, combustible only at a red heat, and even under the most favourable circumstances can only produce by such a combustion an increase of temperature amounting to $305^{0}{\cdot}6$, which in a red heat must necessarily escape altogether observation by the eye."

Satisfied with having obtained the weighty testimony of Professor Bunsen in favour of the facts which I had alleged in confirmation of the theory to which I had given my adhesion, I shall the less regard the opposition that exists between my views and his with respect to the source of the hydrogen evolved.

Professor Bunsen derives this gas from the process in which pyroxenic lava is converted into palagonite through the agency of the

hydrates of the alkalies or alkaline earths, assisted by a high temperature, during which, as he has shown, hydrogen is evolved; and he even shows that if sulphur in vapour be brought into contact with basalt at a high temperature, and afterwards steam be passed over the rock so treated, sulphurous acid is disengaged in the first instance by the union of the sulphur with the oxygen of the peroxide of iron, which metal forms, with another portion of the same body, sulphuret of iron; and that sulphuretted hydrogen will be emitted in the second instance, owing to the decomposition of water, and the union of its hydrogen with the sulphur of the pyrites, whilst its oxygen forms, with the metallic portion, magnetic oxide of iron.

Supposing the formation of palagonite to be going on at all times when sulphuretted hydrogen and pure hydrogen can be shown to be concomitants of the volcanic action, and on a scale commensurate to the amount of gas generated, the explanation of Professor Bunsen will probably be accepted by chemists in general, in preference to that which refers it to the decomposition of water by alkaline and earthy metalloids, or their yet unoxidized sulphurets; but I cannot admit, as a valid objection to this latter hypothesis, the absence of carbonic oxide from volcanic exhalations of which carbonic acid constitutes so large a proportion. No doubt the latter would, as Bunsen remarks, be partially converted into carbonic oxide by hydrogen at the high temperature which probably exists around the *focus* of the volcanic action; but I have always been accustomed to refer the carbonic acid given off by volcanos to the diffusion of heat over contiguous limestone rocks, and not to processes going on at the point where the temperature was most intense.

Nor do I feel quite satisfied with the explanation offered by the Professor, of the presence of sal-ammoniac in the lava, which he refers to the vegetable matter existing in meadow-land overflowed by the molten current. If such were the origin of the volatile alkali, we ought not to find it exhaled round the orifices of the crater, or from any of the fumaroles proceeding directly from the same internal *focus* of action.

It is not my purpose, however, especially on such an occasion as the present, to criticise the labours of this eminent chemist, or to dwell upon those points in which the results of my own humbler inquiries in the same field of research may clash with his. It is sufficient for me to have pointed out to you his Memoirs on the subject of the Iceland Volcanos, as an important present rendered by Chemistry to the sister Science of Geology; and as a service too,

which those who turn away with indifference from researches of a more refined nature, lying strictly within the domain of pure chemistry, would be likely to accept as an undeniable evidence of the extensive utility of our pursuits.

It is, indeed, a fortunate circumstance, in more respects than one, when such happy applications of chemical principles to other departments of natural knowledge are carried out by those of our brethren, who had before established their reputation amongst ourselves, by researches which chemists, and chemists only, are capable of appreciating.

No geologist, at least, can feel, that he has a right to impugn as visionary, conclusions, which have been deduced by a philosopher, who had before attained the first rank amongst experimentalists, by his profound and intricate investigations into the members of the Cacodyle series; just as for the same reason no candid mind can fail to pay deference to the suggestions of another of our foreign associates, on questions relating to physiology, agriculture, and the like; knowing, that before that eminent philosopher had turned his attention to these subjects, he had already earned a great name amongst chemists, by the success with which he had grappled with the most difficult problems in Organic Chemistry; and by the flood of light which he had shed over a class of bodies, before comparatively unattractive, owing to the obscurity which enveloped their real nature, and the absence of those connecting links, the discovery of which by himself, more than perhaps by any other single individual, has shown that they constitute the parts of one harmonious and unbroken series.

And now, Gentlemen, nothing more remains, except that I should express my most cordial thanks to you all, for the kindness and courtesy I have ever experienced since I began to fill the honourable office which you conferred upon me; and to the Members of the Council more especially for relieving me, as they have done, by their close attention to your affairs, from the most onerous portion of my duties. It is also satisfactory to me, on relinquishing the Chair, to reflect, that in selecting Colonel Yorke as my successor, you will place at your head a zealous Member of the Society, who, as being resident amongst you, will have the power, far more efficiently and more regularly than I have found myself able to do, of watching over your interests, and of presiding at your Meetings.

NOTICES

OF

PAPERS CONTAINED IN OTHER JOURNALS.

On the General Distribution of Iodine.

By Stevenson Macadam.

(COMMUNICATED BY THE AUTHOR.)

During the last twelve months I have been engaged in a series of experimental researches as to the general distribution of iodine and bromine.

My attention was first drawn to this subject by the announcement recently made by Chatin, that he had detected the presence of iodine in the atmosphere, in rain-water, and in snow.

Believing that if iodine were present in the media referred to, its neighbour-element bromine would be found there too, I was induced to undertake the investigation, partly with the hope of being able to corroborate the results communicated by Chatin in reference to iodine, but principally with a view to determine whether an appreciable quantity of bromine was present in the atmosphere.

Several minor experiments, in the course of which I subjected to examination quantities of air ranging from 150 to 4000 cubic feet, having given a negative result so far as the detection of iodine and bromine were concerned, I at length undertook an experiment during which 100,000 cubic feet of air were transmitted through—

1st. A tube containing slips of starched paper.

2nd. A gas-bottle containing iron-filings and water, and

3rd. A similar bottle with solution of acetate of lead.

The starched papers and the liquid with iron-filings were intended to retain any *free* iodine, and the lead-solution any soluble iodide. At the conclusion of the experiment, and when 625,000 gallons of air had been passed through the arrangement, it was found that the papers were not sensibly altered in tint, and that neither the water in which the iron-filings were suspended, nor the solution of acetate of lead contained the slightest trace of iodine.

I do not purpose to take up the time of the Society by minutely detailing the several steps of the process to which the liquids obtained at this and other parts of the inquiry were subjected; suffice it to

say, that in every instance when the final testing of the solution was arrived at, I determined the presence or non-presence of iodine by aid of starch, nitrite of potassa, and hydrochloric acid.

Whilst these experiments on the atmosphere were proceeding, I was examining large quantities of rain-water which had fallen in different districts of Scotland.

In some instances, acetate of lead was simply added to the water, and the whole evaporated to dryness; in other cases, iron-filings were first added, and the liquid, after being agitated with an iron rod, was treated with acetate of lead, evaporated to dryness, and subsequently tested. In no instance, even when employing 12 gallons of water at one time, was there any indication of iodine.

Twelve gallons of water obtained from snow collected in the centre of Edinburgh, also 12 gallons from snow which had fallen in the country (at Pennecuick), ten miles south of that city, and 12 gallons from the neighbourhood of Innerleithen, thirty miles south of Edinburgh, were severally treated with iron-filings and acetate of lead, and no iodine was found. The liquids ultimately obtained from the three quantities of snow-water, and which had been used in the starch-testing, were added together, neutralized with an alkali, evaporated to dryness, and carefully charred to decompose the starch; the liquid obtained from this, and which represented 36 gallons of snow-water, did not exhibit the slightest indication of the presence of iodine.

In these experiments I was anxious to employ reagents which were perfectly free from iodine, and therefore refrained from using the fixed alkalies to any extent, although Chatin's papers lead me to believe that they were largely employed by him. The quantity of iodine in potashes seems to decrease by each refinement, but I have never yet encountered a sample of potash in which I did not find iodine when it was sought for. The purest is that obtained by calcining the bitartrate of potash. I have had occasion several times to use small quantities of the alkali thus obtained, and although the presence of iodine could not be detected in 2 ounces of a strong solution, yet in 6 ounces a trace was visible.

The negative results of these experiments lead me to believe that in the air, in the rain-water, and in the snow employed by me, there was not an appreciable quantity of iodine.

Before parting with this part of my subject, I may state that I am well aware that several communications have lately been laid before the Academy of Sciences which tend to verify the accuracy of Chatin's results; but one and all of them are objectionable, from the authors having employed potash and other materials which there is every reason to believe would contain iodine originally.

Marchand employed nitrate of silver, hyposulphite of soda and bicarbonate of potash; Grange, chloroform and caustic potash. Barral, in his late admirable researches on the atmosphere, failed to

detect iodine in the rain-water which falls during January, February, March, April and May, but found a very small quantity in that of June. I have not seen a report of the process employed by him, but think it probable that he used the materials derived from some of his nitric acid experiments, and to which he had added caustic potash in order to fix the nitric acid.

So far as regards the process adopted by myself, it is worthy of remark, that Thénard, in commenting upon the researches of Chatin, recommends that the metals most susceptible of being iodized should be exposed for some time to the action of the air. Some months previous to this suggestion being read to the Academy of Sciences, I had used iron and lead in the search for iodine, and ten days prior to the date of Thénard's paper, a report of some of my experiments was published in the Edinburgh Philosophical Journal, in which the use of the metals was clearly stated.

Every trial for free iodine was accompanied by a search for bromine, but the result was, in every instance a negative one, so far as the atmosphere, rain-water and snow are concerned.

Whilst differing from the views expressed by Chatin in reference to the atmospheric distribution of iodine, I very willingly agree with him in considering that this element will be found more generally distributed in the vegetable kingdom than it has formerly been supposed to be. In 45 plants, hitherto unknown to contain iodine, I have discovered that element. Amongst that number there are representatives from different districts of Scotland, and also different altitudes, from the level of the sea to some 1600 feet above it.

The determination of the presence of bromine in plants is somewhat more difficult, owing to the tests for that element being much less delicate in their action than the starch-test for iodine.

With the exception of the announcement of the presence of bromine in the ammoniacal liquids of the gas works, in plants of the family of *Oscillariæ* growing in thermal waters in the south of France, and a trace in carbonate of potash, I am not aware that the element in question has been shown to be a constituent of inland plants. In the greater number of plants tested by me, not a trace of bromine could be detected; but in potashes, in the ashes of the pear, the gooseberry and the apple-trees, I obtained very distinct evidence of the presence of this element. The tests I relied upon were the odour, the yellow colour imparted to ether, and the production (to a greater or less extent) of the brown-red bromide of gold.

The failures which I encountered when testing for bromine in the majority of plants, I am inclined to ascribe to the small quantity of plant ashes which were at my disposal.

In conclusion, I would state that the presence of iodine and bromine in plants, more especially in the edible ones, implies that these substances are introduced into the system of even the highest animal,

and though as yet unsuccessful, yet I trust that before long I shall be able to determine the presence of both these elements as normal constituents of the animal frame.

On a new Oxide of Hydrogen, and its relation to Ozone.*

By M. Baumert.

This investigation relates chiefly to the volatile substance obtained in the electrolysis of water, and commonly known by the name of ozone. As, however, this body is commonly regarded, without any positive proof, as identical with the substance produced when electric sparks are passed through gases containing oxygen, it became necessary to consider the latter simultaneously with the former. The author, however, abstains from giving any opinion as to the nature of ozone produced by processes not electrical.

Since ozone, as produced by the electrolysis of water, is independent of the substances which are added to the liquid to make it conduct, we may conclude at once that it contains nothing but oxygen and hydrogen. The quantity varies indeed with the nature of the substances so added; but the production never fails when substances are added which are not readily susceptible of any higher degree of oxidation, such as sulphuric, phosphoric, or chromic acid.

That ozone thus obtained contains hydrogen as well as oxygen, may be demonstrated by passing it through a long glass tube, the inner surface of which is coated with a thin film of anhydrous phosphoric acid (this coating is most easily produced by passing through the tube a stream of dry air, carrying with it a quantity of finely-divided phosphoric acid, produced by the recent combustion of phosphorus). If the ozone be perfectly dry, the phosphoric acid will remain unaltered; but if the middle of the tube be gently heated, and the ozone thereby decomposed, the water then formed dissolves the anhydrous phosphoric acid on that side of the flame which is farthest from the end of the tube at which the gas enters, whilst the acid on the other side remains unaltered. It appears, then, that ozone contains the elements of water; and its powerful oxidizing properties show that these elements are combined in it with excess of oxygen.

If, then, a method can be found of estimating the oxygen which, in combination with the elements of water, forms ozone, it will only be necessary in addition to weigh the ozone in its entire state, in order to arrive at a complete knowledge of its composition. The excess of oxygen may be estimated by a method essentially the same as that adopted by Professor Bunsen in the analysis of iodide of nitrogen (see page 90, of this volume). For the oxygen combined

* Pogg. Ann. LXXXIX, 38.

with the elements of water in ozone separates an equivalent quantity of iodine from a solution of iodide of potassium, just as chlorine or bromine does. It is only necessary, therefore, to determine the quantity of iodine thus separated, and the proportionate quantity of oxygen will be known immediately.

A solution of iodine in iodide of potassium is prepared, of such a strength that the quantity of iodine in a degree of the burette shall be only a small fraction of a milligramme $=a$ (*e.g.*, in the following experiments, $=0{\cdot}0002538$ grm.) A quantity of extremely dilute sulphurous acid is also prepared, containing not more than $\frac{3}{1000000}$ of the acid. It is next to be determined how many burette-divisions t, of the iodine-liquid are required to decompose a given volume of this sulphurous acid. The quantity of iodine required for this purpose is $a\,t$. If, now, n measures of this sulphurous acid be added to the iodine-liquid which has been treated with ozone, which latter contains the quantity x of iodine sought, this quantity x will decompose a certain portion of the sulphurous acid. Lastly, if the number of burette-degrees t', and thence the quantity of iodine $a\,t'$ be determined, which is required for the complete decomposition of the n measures of sulphurous acid, we have the equation :

$$x+a\,t'=n\,a\,t,$$

whence

$$x=a\,(n\,t-t').$$

The point at which the decomposition of the acid is complete may be readily ascertained by Dupasquier's method with solution of starch. From this quantity x, which is the quantity of iodine set free by the oxygen in the ozone, the quantity w of oxygen which the ozone contains, in addition to the elements of water, may be readily calculated by the equation

$$w=\frac{O}{I}a\,(nt-t').$$

To determine the total weight of the ozone, it is passed, after being thoroughly dried, into a small bulb-apparatus, containing solution of iodide of potassium, and having attached to it a tube or another bulb-apparatus containing sulphuric acid, to condense the water which evaporates. The increase of weight in this apparatus gives the total weight of the ozone required.

The preparation of the ozone presents considerable difficulties. It acts so rapidly on all organic substances, that any corks or caoutchouc used to connect the different parts of the apparatus are quickly eaten through; hence it is necessary to make all the connections by fusion or by grinding. Notwithstanding this rapid action, the quantity of ozone produced is very small, so that large quantities of water must be decomposed in order to produce the required amount of ozone. In one experiment, in which 76 grms.

of water, acidulated with $\frac{1}{10}$ sulphuric acid were decomposed, 150 litres of detonating gas were found to contain 1 milligrm. of ozone. Chromic acid solutions, containing a little sulphuric acid, yield, however, a larger quantity—viz., about 1 milligrm. in 10 litres of detonating gas. The presence of free hydrogen in the ozoniferous gas must be carefully avoided; otherwise the excess of oxygen in the ozone will combine with the hydrogen, and form water. Hence it is necessary to collect apart the gases evolved at the positive pole—viz., the oxygen and ozone. This is effected by a peculiar arrangement, for a description and figure of which we must refer to the original memoir. The ozoniferous oxygen is then passed through a long tube, containing pieces of pumice-stone soaked in oil of vitriol, and thence into the bulb-apparatus already mentioned, containing the solution of iodide of potassium.

The oxygen, which in the ozone is combined with the elements of water, decomposes the iodide of potassium, setting free an equivalent quantity of iodine, and forming caustic potash. Hence the solution soon assumes a brown colour. This, however, disappears again, because the iodine, thus separated, acts upon the potash, forming iodide of potassium and iodate of potash, which salts, after a while, form a crystalline crust on the dry part of the bulbs. When such a solution, which likewise contains free iodine, is mixed with hydrochloric acid, the iodine of the iodate of potash is again completely separated. Hence the quantity of iodine separated by the oxygen may be determined with equal precision, whether it remains uncombined or forms iodate of potash.

Exp. 1. Current continued for 6 days. Total weight of ozone, $A=0{\cdot}0133$ grms.; $a=0{\cdot}00025387$; $t=55{\cdot}1$, $t'=44{\cdot}4$; $n=10$.

Hence $w=0{\cdot}008109$; $A-w=05191$.

Exp. 2. Current continued for 8 days. Total weight of ozone, $A=0{\cdot}0419$ grms.; $a=0{\cdot}00025387$; $t=246{\cdot}5$; $t'=121{\cdot}8$; $n=3$.

Hence $w=0{\cdot}009887$; $A-w=0{\cdot}005013$.

These numbers agree best with the formula HO_3.

	Calculated.		Found.		
H . . .	1	4	4·34	3·76	4·30
3O . . .	24	96	95·66	96·24	96·00
HO_3	25	100	100·00	100·00	100·00

We have then the following three oxides of hydrogen:

Water . . . . . = HO
Binoxide of hydrogen . = HO_2
Ozone . . . . . = HO_3

From the position which ozone occupies in this series, it might be

regarded as an acid, and called not inappropriately, *hydrogenous* acid. Viewed in this light, it exhibits a certain analogy with nitrous acid. That which is sometimes the case with nitrous acid, appears always to happen with ozone—viz., that it is decomposed by direct contact with bases. Hence it has not yet been found possible to produce any saline compounds of ozone. The chemical relations of this body are, in fact, much more those of a peroxide of hydrogen. Metallic oxides, susceptible of higher oxidation, are converted by it into peroxides and acids. Ammonia is converted into a nitrate, and mercury into mercuric oxide, without forming a salt. On the oxides of the magnesium group of metals it appears to exert no action. The colour of litmus is destroyed by it without previous reddening. Generally, ozone, in contact with easily oxidable substances, gives up its oxygen, and water is separated. This behaviour renders it necessary in preparing ozone, to get rid of the hydrogen simultaneously evolved from the water. Experiments in which detonating gas was passed through the apparatus above described, constantly gave by analysis an excess of water. Now, as in these experiments the other conditions remained the same, this formation of water can only be explained by a direct combination of the free hydrogen with the excess of oxygen in the ozone.

From all that has been said, it may be regarded as certain that hydrogen exists in ozone as an essential constituent. The amount of hydrogen found in the preceding experiments cannot have proceeded from aqueous vapour mechanically carried forward; for the gas, before entering the bulb-apparatus, had passed through a tube containing sulphuric acid five times as long as that which it traversed immediately before emerging from the apparatus. If, then, the increase of weight in the bulb-apparatus had been due to water mechanically carried forwards, it would have been less than the amount corresponding to the weight of oxygen determined by the graduated solution, certainly not greater. Another objection which might be made to these experiments is based upon the tension of the sulphuric acid vapour, which might possibly have been sufficient to carry free sulphuric acid into the iodide of potassium apparatus, together with the gases. To obviate this objection, the author passed 50 litres of atmospheric air in a rapid current through the drying-tube, placing at the end of it a bulb-apparatus filled with distilled water. At the end of the experiment, the water did not show the slightest turbidity with chloride of barium.

Considering the doubt which exists as to the identity of the several bodies included under the general name of ozone, it must be regarded as yet uncertain whether the substance produced by the passage of electric sparks through dry oxygen gas is identical with the compound above examined. If it be so, the formation of the

latter can only be explained by supposing that the dried gas still retains traces of moisture. If, on the contrary, it can be shown that the odorous substance produced by the electric spark in an atmosphere perfectly freed from aqueous vapour, is really oxygen, brought by the enormous but momentary rise of temperature caused by the electric spark, into an allotropic condition characterized by increased combining energy, then it is easy to establish a very simple relation between this allotropic oxygen and the ozone, which has just been shown to be a peroxide of hydrogen. In that case, indeed, the latter must be regarded as water oxidized at the expense of the allotropic oxygen, and must therefore always be formed when this allotropic oxygen comes in contact with water at comparatively low temperatures; the odour of the allotropic oxygen being, in fact, actually due to the formation of ozone. This question will be decided in the affirmative, if we can show that *perfectly* dry oxygen through which the electric spark is passed, actually acquires a combining tendency, strong enough to overcome the most powerful affinities, such as those of chlorine and iodine for potassium, at ordinary temperatures. For this purpose, the apparatus above described was modified as follows:

The ozonized oxygen evolved from the positive pale of the battery was passed, first through a small bulb-apparatus, containing sulphuric acid; thence into a glass tube *a*, surrounded at its middle part with platinum foil, and heated by a spirit-lamp to a temperature sufficient to decompose the ozone, and separate it into water and free oxygen. The gas was made to pass into a bulb *b*, containing pieces of iodide of potassium, and thence into a long tube *c*, filled with chemically pure, anhydrous phosphoric acid. The gas thus freed from ozone and aqueous vapour passed next into a glass tube *e*, the part of which nearest the drying tube *c* was widened, and had two platinum wires inserted through its sides, by means of which a rapid succession of electric sparks from an induction apparatus could be passed through the gas. The inner surface of this tube was coated with a thin film of phosphoric acid, in the manner described on p. 169. Lastly, to the other end of this tube was attached a bulb-apparatus, containing solution of iodide of potassium.

The mode of experimenting was as follows: The ozonized oxygen from the battery was passed for three hours through the apparatus with moderate rapidity, the tube *a* being kept red-hot all the while, and the induction apparatus not being in action. Neither the iodide of potassium in the bulb *b*, nor the phosphoric acid in the tube *e*, exhibited the slightest alteration. Now, the author has found that a film of phosphoric acid attached to the inside of a tube, as above described, will detect the presence of $\frac{1}{10000}$ of a millgrm. of watery vapour; moreover, as 4000 cub. cents. of gas passed through the

apparatus in four hours, it follows that 1 cub. cent. of the gas could not have contained $\frac{3}{10000000}$ of a millgrm. of water. The iodide of potassium in the bulb-apparatus not only remained perfectly colourless, but did not even exhibit a trace of blue colouring on the addition of hydrochloric acid and starch; showing that the ozone had been completely decomposed in passing through the former parts of the apparatus.

The experiment was next repeated, with this difference, that the induction apparatus was set in action, and a rapid succession of sparks passed between the wires in the tube *e*; as, however, a certain quantity of nitrogen had entered into this tube on the previous removal of the bulb-apparatus, the stream of oxygen was continued for a sufficient time to drive it all out before the induction apparatus was set going. Without this precaution, the result might have been vitiated by the formation of nitric acid. In a few minutes after the sparks began to pass the iodide of potassium solution became sensibly yellow, and after an hour, a millgrm. of free iodide could be detected in it. During the whole experiment, the film of phosphoric acid in the tube *e* did not exhibit the slightest change.

The bulb-apparatus was then filled for the third time with fresh solution of iodide of potassium, and any nitrogen that might have entered, expelled as before. The induction apparatus was then set in action, and the experiment repeated in the same manner, excepting that the part of the tube *e* nearest to the bulb *f* was heated by a small spirit-lamp. Under these circumstances, the iodide of potassium solution did not exhibit the slightest change of colour; and even after the lapse of an hour, the addition of hydrochloric acid and starch did not produce the slightest blueing. On detaching the bulb-apparatus, the gas which issued from the tube *e* did not exhibit the faintest odour; but as soon as the spirit-lamp was removed, a very strong smell of ozone became perceptible; ceasing, however, as soon as the passage of the sparks was interrupted, and again becoming perceptible on the instant of their removal.

The quantity of iodine set free in the last experiment but one in the course of an hour, was more than nine times as great as would correspond to any increase of weight in the apparatus resulting from aqueous vapour mechanically carried forward. Hence we may conclude, that there really exists an allotropic oxygen, which, at ordinary temperatures, exhibits a strength of affinity exceeding that of chlorine.

The conditions under which this allotropy of oxygen occurs are very remarkable. In nearly all other bodies, the allotropy produced by elevation of temperature is characterized by diminution of chemical energy. In this case, however, we see a condition distinguished by an increase of combining tendency produced by a rise of temperature of the greatest intensity and shortest duration. It is no less re-

markable, that this state is produced at the highest temperatures only, and when once produced, is destroyed at a temperature of about 200° C. The conversion of allotropic into ordinary phosphorus is not momentary, but requires a certain time. In a similar manner, it is probable that oxygen which has been brought into the allotropic state by the high temperature of the electric spark, may, when quickly cooled, sink from that temperature to 200° without being completely brought back to its original state; provided that the time occupied in the cooling be shorter than that which is required to produce the change within that particular range of temperature. Hence we may understand why it is that so small a fraction only of the total quantity of oxygen remains permanently in the allotropic state, and how this state so quickly disappears at a heat of 200°. The temperature at which ozone is resolved into oxygen and water will probably be found to differ from that at which allotropic oxygen is converted into the ordinary variety. On this point the author hopes to have something further to communicate.

On Piperidine, a New Alkali derived from Piperine.*

By A. Cahours.

Rochleder and Wertheim found† that when a mixture of piperine and soda-lime is heated, an oily volatile base is evolved, possessing all the properties of *Picoline;* this compound they were induced to regard as a pseudo-salt containing the elements of picoline united with a quaternary organic group of atoms.

M. Cahours, being desirous of making a comparative study of picoline and the isomeric base aniline, distilled, according to the recommendation of the chemists above-mentioned, 1 part of piperine with 2½ to 3 parts of potash-lime. The product of the distillation, collected in a cooled receiver, consisted of water, of two distinct volatile bases, and a neutral substance possessing an agreeable aromatic odour, like that of the derivatives of the benzoic series. When this crude liquid is treated with fragments of caustic potash, a light oily substance separates, having a strongly ammoniacal odour, and dissolving in all proportions in water. This oil, when distilled, passes over almost wholly between 105° and 108° C.; but towards the end of the distillation, the thermometer rises rapidly to 210°, and there remains stationary. The more volatile product, which forms more than $\frac{9}{10}$ of the crude liquid, distils over entirely at 106°, when rectified anew. This substance, which possesses all the characters of a definite compound, is a colourless, very limpid liquid, having a strong

* Ann. Ch. Phys. [3] XXXVIII, 76. † Ann. Ch. Pharm. LXX, 58.

ammoniacal odour, but recalling also that of pepper; it blues reddened litmus strongly, has a very caustic taste, and saturates the most powerful acids. It dissolves in all proportions in water, to which it communicates very decided alkaline properties. The solution behaves like ammonia with saline solutions, excepting that it does not appear to redissolve the oxides of copper and zinc.

By reason of its origin, the author designates this base by the name of *Piperidine*.

The analysis gave the following results:

	Calculation.		Experiment.			
			I.	II.	III.	IV.
10 C . .	60	70·58	70·46	70·31	—	70·48
11 H . .	11	12·94	12·96	13·03	—	13·05
N . .	14	16·48	—	—	16·60	—
$C_{10}H_{11}N$ . .	85	100·00				

From these numbers it appears that the simplest formula by which the composition of the base can be expressed is $C_{10}H_{11}N$; to determine whether the rational formula is really expressed by these numbers or by a multiple of them, the vapour-density was taken. Experiment showed it to be 2·958. Now supposing that the preceding formula represents 4 vols. of vapour, we have:

10 vols.	Carbon-vapour	= 8·440
22 „	Hydrogen . .	= 1·522
2 „	Nitrogen . .	= 1·944
		11·906

$$\frac{11{\cdot}906}{4} = 2{\cdot}976$$

The equivalent of piperidine is therefore actually represented by the formula

$$C_{10}H_{11}N.$$

This base forms perfectly crystalline compounds with hydrochloric, hydrobromic, hydriodic, sulphuric, nitric and oxalic acids.

The *Hydrochlorate*, $C_{10}H_{11}N$, HCl, forms long colourless needles, very soluble in water and alcohol; from the alcoholic solution it separates in long prisms. The crystals volatilize when moderately heated, and are not altered by exposure to the air.

Hydrochlorate of piperidine forms with chloride of gold a crystalline powder, composed of small needles of a fine yellow colour, and with bichloride of platinum a compound which crystallizes in orange-coloured needles, having the composition $C_{10}H_{11}N$, HCl, $PtCl_2$. This salt is very soluble in water, less soluble in alcohol.

Hydriodate of Piperidine, $C_{10}H_{11}N$, HI, crystallizes in long needles, resembling the hydrochlorate.

Nitrate of Piperidine, $C_{10}H_{11}N$, HNO_6, forms small crystalline needles. It is obtained by saturating the base with weak nitric acid, and evaporating *in vacuo*. It is decomposed by heat, giving off vapours which have an aromatic odour. Alcohol dissolves it readily.

Nitrous acid acts violently on piperidine, forming a heavy aromatic liquid, which the author did not obtain in quantity sufficient for analysis. From the results obtained by Hofmann,* on the mutual action of nitrous acid and aniline, it is probable that the action just mentioned gives rise to the formation, first of the compound $C_{10}H_{10}O_2$, and then of $C_{10}\left.\begin{matrix}H_9\\NO_4\end{matrix}\right\}O_2$.

Oxalate of Piperidine, $C_{10}H_{11}N$, C_2HO_4, is formed by saturating piperidine with a solution of oxalic acid; it separates by evaporation in delicate needles, which may be obtained pure by a second crystallization.

Sulphate of piperidine, $C_{10}H_{11}N$, HSO_4, obtained directly by saturating piperidine with sulphuric acid, is a crystallizable salt, deliquescent, and therefore very soluble in water.

Piperidic Urea.—When sulphate of piperidine is boiled with an equivalent quantity of cyanate of potash, sulphate of potash is formed, together with a compound analogous to urea:

$$C_{10}H_{11}N,\ HSO_4 + C_2NKO_2 = KSO_4 + C_{12}H_{12}N_2O_2.$$

To separate the latter compound, the liquid is evaporated to dryness, the residue digested in strong alcohol, and the alcoholic solution left to evaporate; the piperidic urea is then deposited in long white needles:

	Calculation.	Mean of experiments.
12 C . . .	72	56·25	56·32
12 H . . .	12	9·37	9·41
2 N . . .	28	21·87	22·05
2 O . . .	16	12·51	—
$C_{12}H_{12}N_2O_2$ . .	128	100·00	

This compound is also formed when cyanic acid vapour is passed into piperidine. A solid mass is then obtained, soluble in water and alcohol, and possessing all the characters of the compound just described.

If, instead of cyanic acid vapour, cyanate of methyl be passed into the solution, an analogous compound is obtained, which bears the same relation to the preceding that methyl-urea bears to ordinary urea:

* Chem. Soc. Qu. J. III, 231.

This latter compound is in fact, *Piperidic Methyl-urea* $= C_{12}\left\{\begin{matrix} H_{11} \\ C_2H_3 \end{matrix}\right\} N_2O_2$; its formation is expressed by the equation $C^2N\ (C_2H_3)\ O_2 + C_{10}H_{11}N = C_{14}H_{14}N_2O_2$. Similarly, cyanate of ethyl with piperidine forms *Piperidic Ethyl-urea* $= C_{16}H_{16}N_2O_2 = C_{12}\left\{\begin{matrix} H_{11} \\ C_4H_5 \end{matrix}\right\} N_2O_2$

Benzopiperidine, $C_{34}H_{15}NO_2$.—When chloride of benzoyl is made to act on piperidine, a large quantity of heat is evolved, and hydrochlorate of piperidine is formed, together with an oily, heavy liquid, which may be easily freed from the hydrochlorate by washing with acidulated water. When left to itself, it soon solidifies; and when the solid mass is dissolved in alcohol, which dissolves it readily, and the solution evaporated, the new compound separates in the form of beautiful colourless prisms analogous to benzamide.

		Calculation.	Mean Experiments.
24 C	144	76 18	75·90
15 H	15	7·94	8·11
N	14	7·41	7·57
2 O	16	8·47	—
$C_{24}H_{15}NO_2$	189	100·00	

The formation of this compound may be represented by the equation:

$$2\,C_{10}H_{11}N + C_{14}H_5O_2Cl = C_{12}H_{11}N,\,HCl + C_{24}H_{15}NO_2,$$

Cumylopiperidine, $C_{30}H_{11}NO_2$.—Obtained in a similar manner by the action of chloride of cumyl on piperidine.

Chloride of acetyl appears also to exert a similar action.

Sulphocarbonate of Piperidine, $C_{10}H_{11}N, CS_2$.—When bisulphide of carbon is added drop by drop to piperidine, a very rapid action takes place, and the mixture becomes very hot. No gas is however disengaged, neither is the slightest formation of sulphuretted hydrogen perceptible. The liquids must be mixed cautiously, otherwise a portion of the contents of the vessel will be thrown out. If, when the action is terminated (the sulphide of carbon having been used in excess), the solid mass be taken up by alcohol, which dissolves it readily, especially when hot, and the solution left to evaporate, the compound separates, sometimes in fine needles, sometimes in crystals of considerable size, having the form of a symmetrical oblique prism.

	Calculation.		Experiment.
11 C	66	53·65	53·61
11 H	11	8·94	8·90
N	14	11·38	—
2 S	32	26·03	25·90
$C_{10}H_{11}N, CS_2$	123	100·00	

Methylopiperidine, $C_{12}H_{13}N$.—Formed by the action of iodide of methyl on piperidine. The iodide of methyl must be added drop by drop, and the tube cooled while the mixing is going on; otherwise, a portion of the contents will be thrown out. If the liquids are mixed in equal volumes, there is formed a beautiful white crystalline mass, which is soluble in water, and when treated with potash, yields an oily liquid, also soluble in water; this oily liquid has an ammoniacal odour like that of piperidine, but more aromatic. After being digested with fragments of caustic potash, and then rectified, the new product assumes the form of a colourless, very mobile liquid, having an ammoniacal and aromatic odour, soluble in water, boiling at 118° C, and forming crystallizable compounds with acids. This compound is methylopiperidine, its formation is expressed by the equation:

$$C_{10}H_{11}N + C_2H_3I = HI,\ C_{12}H_{13}N.$$

		Calculation.	Experiments.
12 C . . .	72	72·72	72·83
13 H . . .	13	13·13	13·74
N . . .	14	14·15	14·35
$C_{12}H_{13}N$	99	100·00	100·42

The vapour-density is found by experiment to be 3·544; and supposing that the preceding formula represents 4 volumes of vapour, the calculated density is 3·513.

Methylopiperidine forms with hydrochloric acid, a salt which crystallizes in beautiful colourless needles. The solution of this salt forms with bichloride of platinum, a compound soluble in water and more soluble in alcohol; when the alcoholic solution is left to evaporate, the salt separates, sometimes in needles, sometimes in tables of a fine orange colour. The formula of this salt is $C_{12}H_{13}N$, HCl, $PtCl_2$.

Methylopiperidine, in contact with iodide of methyl becomes slightly heated, and the mixture, if heated in a a sealed tube, finally solidifies. On dissolving the product in alcohol and leaving the solution to evaporate, magnificent crystals are obtained, which become very brilliant after being dried on bibulous paper. These crystals, when distilled, partly volatilize and are partly decomposed into methylopiperidine and iodide of methyl.

14 C . . .	84	35·00	34·90
16 H . . .	16	6·67	6·75
N . . .	14	5·83	5·92
I . . .	126	52·50	—
$C_{14}H_{16}N,I$	240	100·00	

Ethylopiperidine, $C_{14}H_{15}N$.—Piperidine becomes strongly heated by contact with iodide of ethyl, but not so much as with iodide of

methyl. The mixture, heated in sealed tubes in the water-bath, solidifies into a mass of fine white crystals, which, when decomposed by potash, yield an oil, the odour of which resembles that of piperidine, but is less ammoniacal and more aromatic. This liquid, which is colourless, and very mobile, boils at 128°. Its density is less than that of water. It is soluble in water, but less so than piperidine. Pieces of potash added to the solution effect the complete separation of the base. Alcohol and ether dissolve it readily.

		Calculation.	Mean Experiment.
14 C . . .	84	74·33	74·16
15 H . . .	15	13·27	13·19
N . . .	14	12·40	12·59
$C_{14}H_{15}N$ . . .	113	100·00	

The vapour-density is by experiment, 3·986; by calculation, supposing the formula to represent 4 vols. of vapour, 3·959.

The *hydrochlorate of ethylopiperidine* crystallizes in beautiful needles, possessing considerable lustre. Their formula is $C_{14}H_{15}N$, HCl.

When a concentrated solution of this salt is mixed with a concentrated solution of bichloride of platinum, a copious precipitate is formed, which dissolves in a larger quantity of water, especially if hot. If it be redissolved in a mixture of equal parts of water and alcohol, and the solution left to evaporate, the salt separates in large, beautiful, orange-coloured prisms.

Ethylopiperidine scarcely becomes heated by contact with iodide of ethyl. When the liquids are enclosed in a sealed tube, the iodide of ethyl in excess, and heated for several hours in the water-bath, a viscid mass is obtained, which floats upon the hydriodic ether. Water dissolves it readily, and in all proportions; the solution does not crystallize *in vacuo*. When it is treated with oxide of silver recently precipitated and washed, a deposit of iodide of silver is obtained, and a liquid which, when evaporated *in vacuo*, yields very deliquescent crystals, having a bitter taste and a strong alkaline reaction. These crystals, when strongly heated, decompose, giving off an inflammable gas and ethylopiperidine; they dissolve in hydrochloric acid, with evolution of heat. The liquid being concentrated by heat, or better, by evaporation *in vacuo*, yields a very deliquescent salt, which crystallizes in scales. The solution of the hydrochlorate forms a copious precipitate in a strong solution of bichloride of platinum. If very dilute and boiling solutions be used, the mixture on cooling deposits orange-coloured crystals, very much like those of chloroplatinate of potassium. The composition of this platinum-salt is as follows:

	Calculation.		Experiment.
18 C . . .	108	31·17	31·01
20 H . . .	20	5·76	5·82
3 Cl . . .	106·5	30·73	
N . . .	14·0	4·06	
Pt . . .	98·0	28·28	28·26
$C_{18}H_{19}N$, HCl, $PtCl^2$.	246·5	100·00	

Amylopiperidine, $C_{20}H_{21}N$.—Iodide of amyl scarcely becomes heated by contact with piperidine; but the mixture soon solidifies when heated in the water-bath in sealed tubes. If, after the action has gone on for several days, the crystals be dissolved in a small quantity of water and the liquid distilled in contact with fragments of caustic potash, a limpid liquid passes over, having both an ammoniacal and an amylic odour. This compound, after being dried by fused caustic potash, and then redistilled, forms a colourless liquid, which boils at 186°, but is less soluble in water than the corresponding ethyl and methyl compounds. It forms crystallizable salts with acids.

	Calculation.		Experiment.
20 C . . .	120	77·41	77·54
21 H . . .	21	13·55	13·64
N . . .	14	9·04	9·17
$C_{20}H_{21}$, N . .	155	100·00	

The vapour-density is by experiment 5·477; by calculation, supposing the equivalent to represent 4 vols. of vapour, it is 5·452.

Hydriodate of amylopiperidine forms large, white, shining laminæ.

When a solution of bichloride of platinum is poured into a hot solution of hydrochlorate of amylopiperidine, dark, orange-coloured, oily drops are deposited, which solidify in a few hours, presenting a crystalline aspect. On dissolving this product in dilute alcohol, and evaporating slowly, the platinum-salt separates in very hard prisms, often of considerable size, and of a fine orange colour, even when the quantity of material operated upon is small. The formula of the salt is $C_{20}H_{21}N$, HCl, $PtCl_2$.

The reactions of piperidine above described might lead to the supposition that it is a base belonging to the amylene series, and formed from amylene, $C_{10}H_{10}$, by the substitution of NH_2 for H, or as a compound ammonia formed by the substitution of the radical $C_{10}H_9$ for one of the atoms of hydrogen; according to the latter supposition, its rational formula would be $\left.\begin{matrix} C_{10}H_9 \\ H \\ H \end{matrix}\right\}$N. This view of its composition would agree very well with the results obtained by

treating it with the iodide of methyl and ethyl. To test the truth of this hypothesis, M. Cahours examined the action of bromide of amylene, $C_{10}H_{10}Br_2$, on an alcoholic solution of ammonia. The two liquids mix easily at ordinary temperatures, without producing any particular result; and even when they were heated together in a sealed tube for several days, the only products obtained were hydrobromate of ammonia and the compound $C_{10}H_9Br$, together with a very small quantity of an oily liquid having an ammoniacal odour; neither was any particular action produced by treating an alcoholic solution of ammonia with the compound $C_{10}H_9Br$, or with the corresponding compounds C_4H_3Br, C_6H_5Br, C_8H_7Br.

From these negative results it would appear that the radical $C_{10}H_9$, and the analogous compounds C_4H_3, C_6H_3, &c., are not capable of replacing either of the atoms of hydrogen in ammonia. The author is therefore disposed to regard piperidine as an imidogen-base, resulting from the substitution of two binary molecular groups for 2 atoms of hydrogen in ammonia; according to this view, its formula may be written as follows:

$$C_{10}H_{11}N=N\begin{cases}H\\C_xH^y\\C_{10-x}H_{10-y}\end{cases}$$

The author's experiments have not yet enabled him to determine the values of x and y; but the composition of the base is perhaps that which is represented by the formula,

$$N\begin{cases}H\\C_4H_5\\C_6H_5\end{cases}$$

the hydrogen being replaced partly by ethyl, partly by allyl; this however is at present a pure hypothesis, not founded on any experiment. The general properties and basic power of piperidine show that it occupies an intermediate place between aniline and Wurtz's ammoniacal bases, approaching, however, more nearly to the former. From picoline, with which Rochleder and Wertheim had compared it, it differs in every respect.

Researches on the Oxygen-Radicals.

By L. Chiozza.*

The recent investigations of Gerhardt on the anhydrous monobasic acids,† have clearly shown that these acids contain, in a duplicate form, those oxygenated groups of atoms which are contained as one atom in the ordinary hydrated acids.

* Ann. Chem. LXXXIV, 102; Comp. rend. XXXV, 225.
† Chem. Soc. Qu. J. V, 127, 226.

The process by which benzoic benzoate, cuminic cuminate, &c., were prepared, naturally leads to the expectation that the radicals themselves may be obtained by causing the chlorides of these oxygenated groups of atoms to act on the metallic compounds derived from the corresponding aldehydes. This expectation is fully confirmed by the following experiments.

When cuminol is heated with potassium in a small, covered platinum crucible, a product is obtained having the composition $C_{10}H_{11}O$.* It may be purified from undecomposed cuminol by pressure between filtering-paper, and subsequent exposure over oil of vitriol *in vacuo*.

The substance thus obtained, when brought in contact with an equivalent quantity of chloride of cumyl, soon becomes liquid, and forms a homogeneous mixture, which, when the temperature is slightly raised, becomes pasty from separation of chloride of potassium. The mass is then to be treated, first with water, then with a solution of carbonate of potash, and finally shaken up with ether. A stratum of ether, containing the whole of the cumyl, soon rises to the surface of the liquid; it is removed by a pipette, and the ether driven off by a gentle heat. To free the product completely from the water which it contains, it must however be heated till it begins to give off vapours.

The action which takes place between the compound $C_{10}H_{11}KO$ and the chloride of cumyl, is expressed by the following equation:

$$\left\{\begin{matrix} C_{10}H_{11}O \\ K \end{matrix}\right\} + \left\{\begin{matrix} C_{10}H_{11}O \\ Cl \end{matrix}\right\} = \underbrace{\left\{\begin{matrix} C_{10}H_{11}O \\ C_{10}H_{11}O \end{matrix}\right\}}_{\text{Cumyl.}} + KCl.$$

Cumyl presents the appearance of a thick oil, heavier than water. At ordinary temperatures its odour is faint, but when gently heated, it gives off an agreeable odour like that of geraniums. In this respect it resembles benzoyl, $\left\{\begin{matrix} C_7H_5O \\ C_7H_5O \end{matrix}\right\}$ the compound which Ettling and Stenhouse obtained by the dry distillation of benzoate of copper.

Cumyl is difficult to inflame, and burns with a smoky flame. In a mixture of ice and salt, it solidifies, forming a colourless, amorphous mass. On being again raised to the ordinary temperature of the air, it recovers its fluidity. It dissolves with tolerable facility in boiling alcohol, but very sparingly in cold alcohol. Cumyl boils at a temperature above 300°, decomposing at the same time into cuminic acid and other less oxygenated products, while a carbonaceous residue remains in the retort.

Cumyl gives by analysis numbers corresponding to the formula, $C_{20}H_{22}O_2$.

* Gerhardt's Notation. See papers last cited.

When cumyl is heated with a small quantity of hydrate of potash, cuminate of potash is formed, and the strong, characteristic odour of cumal is evolved.

$$\left\{\begin{matrix}C_{10}H_{11}O\\C_{10}H_{11}O\end{matrix}\right\}+\left\{\begin{matrix}H\\K\end{matrix}\right\}O=\left\{\begin{matrix}C_{10}H_{11}O\\K\end{matrix}\right\}+\left\{\begin{matrix}C_{10}H_{11}O\\H\end{matrix}\right\}O.$$

The author endeavoured by similar means to form cumyl-benzoyl, $\left\{\begin{matrix}C_{10}H_{11}O\\C_{7}H_{5}O\end{matrix}\right\}$ and cumyl-acetyl (or cumyl-othyl) $\left\{\begin{matrix}C_{10}H_{11}O\\C_{2}H_{3}O\end{matrix}\right\}$; but the experiments have not yet led to any satisfactory result.

On Anhydrous Organic Acids.

By L. Chiozza.*

Valerianic Acid.—When valerianate of potash, purified by evaporating its alcoholic solution to dryness, and heating the residue till it begins to melt, is brought in contact with oxychloride of phosphorus, a violent action immediately takes place; the insupportable odour of the oxychloride is destroyed, and the mixture is converted into a saline mass, saturated with a viscid, faintly-smelling oil. The latter substance is *Valerianic Valerianate*, or *Anhydrous Valerianic Acid.* To obtain it pure, it must be treated, first with a very dilute solution of carbonate of potash, then with ether, and the ethereal solution, after being shaken up with chloride of calcium, left to evaporate over the water-bath.

The substance, thus purified, gave by analysis numbers agreeing exactly with the formula $C_{10}H_{18}O_3$.

Anhydrous valerianic acid is a colourless, tolerably mobile oil, lighter than water. When recently prepared, it has a faint, and by no means unpleasant odour, like that of apples; but if rubbed on the hands, it imparts to them the odour of valerianic acid, which lasts for several days. The vapour attacks the eyes, and excites coughing. Boiling water slowly converts the oil into hydrated valerianic acid. The same transformation is quickly effected by alkaline solutions, and instantly by fused potash.

The anhydrous acid boils at 215°, distilling over in the form of a colourless liquid like water.

The formation of anhydrous valerianic acid is explained as follows: Oxychloride of phosphorus converts a portion of the valerianate of potash into phosphate of potash and *chloride of valeryl*, as shown in the following equation:

$$3\left[\left\{\begin{matrix}C_5H_9O\\K\end{matrix}\right\}O\right]+PCl_3O=PK_3O_4+3\underbrace{(C_5H_9O,Cl)}_{\text{Chloride of Valeryl.}}$$

* Ann. Ch. Pharm. LXXXIV, 106; LXXXV, 229.

But the chloride of valeryl acts in its turn on the valerianate of potash, in such a manner, that the final products of the reaction are phosphate of potash, chloride of potassium, and anhydrous valerianic acid.

$$3\left[\begin{matrix}C_5H_9O\\Cl\end{matrix}\right]+3\left[\begin{matrix}C_5H_9O\\K\end{matrix}\right\}O\Big]=3\,ClK+3\left[\begin{matrix}C_5H_9O\\C_5H_9O\end{matrix}\right\}O\Big]$$

Benzoic Valerianate, or *Valerianic Benzoate*, $\begin{matrix}C_5H_9O\\C_7H_5O\end{matrix}\Big\}O$. — This compound is readily obtained by the action of chloride of benzoyl on valerianate of potash. It is an oil, heavier than water, neutral to test-paper, and having an odour very much like that of valerianic acid. Its vapour is pungent, and excites tears. Alkaline liquids convert the oil into benzoate and valerianate of the alkali.

Benzoic valerianate is resolved by distillation into anhydrous benzoic and anhydrous valerianic acid. This decomposition does not, however, take place so quickly as that of benzoic acetate;* and to obtain the anhydrous valerianic acid, it is necessary to rectify the product several times.

The property which anhydrous acids possess of forming amides or anilides, when they act on ammoniacal gas or on aniline, furnished the author with the means of preparing a new compound, viz.:

Valeranilide.—This compound is in fact produced when anhydrous valerianic acid is brought in contact with aniline. It crystallizes in splendid, elongated, rectangular laminæ, which have a strong lustre, and fuse at 115°. It is slightly soluble in boiling water, in which also it melts into clear drops. At a temperature above 220°, it distils over for the most part unchanged. Alcohol and ether dissolve it readily. A concentrated and boiling solution of caustic potash acts on it very slowly; fused hydrate of potash causes a perceptible evolution of aniline.

The crystallization of this compound exhibits a remarkable circumstance, already observed by Gerhardt in the crystallization of formanilide. When valeranilide separates from its solution in boiling dilute alcohol, it often takes the form of oily drops, which remain permanent for several hours, even after the liquid has become perfectly cold; but on a slight movement of the vessel, the whole mass solidifies almost instantly to a group of fine needles.

The analysis of valeranilide yields numbers which agree perfectly with the formula, $C_{11}H_{15}NO$.

Anhydrous Caprylic Acid. — Hydrated caprylic acid was prepared by Fehling's method from cocoa-nut-oil, and separated from the caproic acid which accompanied it, by neutralizing with caustic

* Chem. Soc. Qu. J. V, 225.

baryta, and purifying the caprylate of baryta, which crystallizes out first, by several recrystallizations.

This baryta-salt is very easily attacked by oxychloride of phosphorus, the action being attended with but a slight elevation of temperature, and the mixture changing to a pasty mass, from which the anhydrous caprylic acid may be easily separated by ether free from alcohol. The ethereal solution is then treated with weak potash, then dried over chloride of calcium, and the ether driven off by the heat of the water-bath.

Anhydrous caprylic acid (caprylic caprylate), thus obtained, gave by analysis numbers agreeing perfectly with the formula,

$$C_{16}H_{30}O_3 = \left.\begin{matrix} C_8H_{15}O \\ C_8H_{15}O \end{matrix}\right\} O.$$

It is a colourless, very mobile oil, greasy to the touch, and lighter than water. Its odour is repulsive. When heated, it gives off vapours which irritate the throat strongly, and have an odour more aromatic than that of the oil. In a mixture of ice and salt, it solidifies to a white mass, which appears crystalline only when examined by the microscope. At a few degrees below 0°, it recovers its fluidity. Boiling-point about 280°, but rising towards the end of the distillation to 290°, the residue in the retort at the same time assuming a darker colour, and giving off empyreumatic, disagreeably smelling products.

When anhydrous caprylic acid is brought into contact with aniline, the mixture becomes slightly heated, and in a few days solidifies to a buttery mass. It is probable that the product of this action is *Caprylanilide*, or at least that this substance is one of the products formed thereby; but the tendency of the mass to retain the liquid state renders it very difficult to obtain a pure product.

Boiling water has no action on anhydrous caprylic acid. This substance may indeed be distilled with water, without exhaling any odour of hydrated caprylic acid; it is, however, partially converted into the hydrate by long exposure to the air. Moderately strong potash-ley converts it, when warmed, into caprylate of potash.

We see then that, whereas anhydrous acetic acid is converted into the hydrated acid by mere contact with water, and anhydrous valerianic acid quickly absorbs water when simply exposed to moist air, caprylic acid, which is a higher member of this group of homologous acids, shows so little tendency to unite with water, that the intervention of caustic alkalies is necessary to convert it into the hydrate. Anhydrous pelargonic acid exhibits this resistance to reagents in a still higher degree.

Anhydrous Pelargonic Acid.—Prepared in a similar manner to the compound last described. Colourless oil, lighter than water.

In the cold, its odour is faint, like that of rancid butter; but when put into boiling water it imparts to the watery vapour an aromatic, slightly vinous odour, which is not at all unpleasant. Heated by itself upon glass, it emits pungent vapours, which smell like burnt fat.

At 0° C. it solidifies in a mass of fine needles, which melt again at 5°. Its analysis gave numbers agreeing exactly with the formula,

$$C_{18}H_{34}O_3 = \left.\begin{matrix} C_9H_{17}O \\ C_9H_{17}O \end{matrix}\right\} O.$$

Benzoic Pelargonate, or *Pelargonic Benzoate,* $C_{16}H_{22}O_3 = \left.\begin{matrix} C_7H_5O \\ C_9H_{17}O \end{matrix}\right\} O$.—Colourless oil, heavier than water, and closely resembling anhydrous pelargonic acid in its physical properties. At a few degrees below 0° C. it changes to a buttery mass, which immediately resumes its liquid form when taken out of the freezing mixture. When heated, it gives off highly pungent vapours, and decomposes at a high temperature, yielding anhydrous benzoic and anhydrous pelargonic acid, accompanied by a few other products resulting from the decomposition of the latter. The change which this substance undergoes, when heated, may be understood by exposing it to the action of cold; there is then formed a crystalline precipitate, which does not redissolve till the mixture is stirred.

A drop of benzoic pelargonate, when left to itself in moist air, yields delicate crystals of benzoic acid. With alkalies, benzoic pelargonate yields a benzoate and a pelargonate.

On Sinapine.*

By MM. Babo and Hirschbrunn.

The process employed by the authors for separating sinapine from mustard is as follows: A considerable quantity, at least 25 lbs., of mustard (Dijon mustard), is compressed to extract the oil, and the residue exhausted successively, by cold alcohol and hot alcohol of 85 per cent. The alcoholic liquors are mixed together, and distilled to about three-fourths, till a portion of the residue separates on cooling into two equal layers, the upper of which is an oil, and the lower an alcoholic solution of sulphocyanide of sinapine.† Sometimes this lower stratum solidifies to a magma of crystals of sulphocyanide of sinapine; sometimes the crystallization may be brought about by the addition of small quantities of water; but in most cases a syrupy liquor is obtained, which only deposits the sulphocyanide of sinapine after careful evaporation.

* Ann. Ch. Pharm. LXXXIV, 10; Ann. Ch. Phys. [3] XXXVIII, 108.

† The substance which the authors call *sulphocyanide of sinapine* is that which is commonly regarded as *sinapine* itself (vid. p. 191.)

There is considerable difficulty in seizing the point at which the distillation ought to be stopped. If the concentration be not carried far enough, the oil which separates still contains alcohol and sinapine. In this case it is best to heat the oil gently, and add to it an alcoholic solution of sulphocyanide of potassium.

The sulphocyanide of sinapine crystallizes after a few days. The crystals are separated from the somewhat viscid mother-liquid by filtration through cloth and by pressure, and then dissolved in warm alcohol of 90 per cent. The solution, on cooling, yields crystals which are to be dissolved in boiling water; and the aqueous solution, after decolorization by animal charcoal, deposits on cooling yellowish, silky needles, united in tufts. These crystals, which resemble those of sulphate of quinine, dissolve slowly at ordinary temperatures, but readily with the aid of heat in alcohol and in water. The solutions have generally a yellowish tint, but become perfectly colourless on the addition of a drop of acid.

Sulphocyanide of sinapine, when pure and dry, may be heated to 130° without alteration. At this temperature it melts into a yellow liquid, which, on cooling, is transformed into a vitreous mass; at a higher temperature, it decomposes, giving off vapours which have a very unpleasant odour, and contain an alkaloid, probably methylamine. Its analysis gave the following results:

	Calculation.		Experiment.		
			I.	II.	III.
34 C	204	55·29	56·01	55·16	55·09
25 H	25	6·77	6·77	6·88	6·75
2 N	28	7·58	6·91	7·93	7·80
2 S	32	8·67	8·81	9·13	
10 O	80	21·69			
$C_{34}H_{25}N_2S_2O_{10}$	369	100·00			

These results differ considerably from those obtained by Henry and Garot.

Sulphocyanide of sinapine does not appear to combine directly with other bodies, but exhibits the following reactions:

Hot strong sulphuric acid dissolves it, blackening at the same time, and giving off hydrosulphocyanic acid. When a solution of sulphocyanide of sinapine in dilute sulphuric or in hydrochloric acid, is evaporated, hydrosulphocyanic acid is likewise evolved, and a liquid is obtained in which crystals form. Nitric acid instantly imparts to sulphocyanide of sinapine a deep red colour. On heating the liquid, the colour changes to yellow, and sulphuric acid may afterwards be detected in the solution.

Alkalies dissolve sulphocyanide of sinapine, forming a liquid of a deep yellow colour. This reaction is very delicate, and is produced

by most alkaline substances. On adding an acid to the alkaline solution, if not too dilute, the sulphocyanide of sinapine is reprecipitated. On the other hand, the solution is decomposed by boiling, and the addition of an acid gives rise to the formation of a crystalline compound, which constitutes a new substance. When the solution of sulphocyanide of sinapine is boiled with baryta-water, the liquid becomes decolorized, and a yellowish baryta-compound is separated, from which hydrochloric acid separates the crystalline compound just mentioned. The solution contains hydrosulphocyanic acid.

Under these circumstances, there is formed by the action of alkalies on sinapine, a weak acid, to which the authors give the name of SINAPIC ACID; it is prepared as follows:

Pure sulphocyanide of sinapine is dissolved in potash, and the solution, at a boiling-heat, supersaturated with hydrochloric acid. The resulting precipitate is purified by dissolving it several times in alcohol of 60 per cent. Sinapic acid is then obtained, crystallized in small prisms, slightly soluble in cold water and alcohol, more soluble in these liquids when hot, insoluble in ether. This acid combines with bases; the salts which it forms with the alkalies are crystallizable, but all, excepting the baryta-salt, are very unstable.

22 C . . .	132	58·93	58·67	58·92
12 H . . .	12	5·35	4·87	5·67
10 O . . .	80	35·72	36·46	35·41
C_{22} H_{12} O_{10} . .	224	100·00	100·00	100·00

The formula of the baryta-salt is 2 BaO, C_{22} H_{10} O_8.

The solution of this substance in potash or soda changes very rapidly on exposure to the air, especially when it is neutral; it first becomes red, then green, and ultimately brown. Sinapate of potash forms white precipitates with chloride of calcium, chloride of barium, and alum; it precipitates and reduces the solutions of mercury, silver, and gold.

Heated to 150° or 200° C., it melts, and at a higher temperature decomposes, yielding an oil, which has not yet been analyzed. With nitric acid, it behaves like sulphocyanide of sinapine. In its composition and properties, it exhibits a close analogy with erythric acid, as described by Schunck and Stenhouse.

SINCALINE.—Sinapic acid is not the only product of the action of alkalies on sinapine; for there is likewise found an alkaloid, to which the authors give the name of *Sincaline*. It is isolated as follows:

A considerable quantity of sulphocyanide of sinapine is heated with baryta-water, till all the sinapic acid is deposited in the form of a baryta-salt. The solution, filtered and acidulated with sulphuric acid, is then mixed with a solution of protosulphate of iron and sulphate of copper. The sulphocyanide of copper, which precipitates, is then separated by filtration, the liquid treated with excess of

baryta-water to precipitate the oxides of iron and copper, and the excess of baryta separated by carbonic acid. The filtered solution, evaporated over the water-bath, yields a deliquescent crystalline mass of carbonate of sincaline.

To separate the alkaloid, the carbonate is converted into hydrochlorate, and the latter salt is decomposed by oxide of silver. By evaporating the filtered liquid, a colourless or slightly brown crystalline mass is obtained, which very rapidly absorbs moisture and carbonic acid from the air. This alkaloid, in many of its reactions, behaves like caustic potash. It precipitates all the metallic oxides, redissolving alumina and oxide of chromium when added in excess. It dissolves sulphur, forming a sulphide and a hyposulphite. It is not volatile, but is decomposed by dry distillation, giving off inflammable vapours, with an odour like that of methylamine.

Sincaline forms crystallizable but deliquescent compounds with hydrochloric, sulphuric, nitric, and carbonic acids. The authors have analyzed the double salts which hydrochlorate of sincaline forms with the chlorides of gold and platinum. These compounds are crystallizable, and composed as follows:

Double Hydrochlorate of Sincaline and Platinum.

	Calculation.		Experiment.	
			I.	II.
10 C	60·0	19·34	19·73	19.58
15 H	15·0	4·83	5·16	5·10
N	14·0	4·73		
2 O	16·0	4·96		
3 Cl	106·5	34·33		
Pt	98·7	31·81	31·36	
	310·2	100·00		

Double Hydrochlorate of Sincaline and Gold.

	Calculation.		Experiment.
10 C	60·0	13·50	13·63
15 H	15·0	3·38	3·38
N	14·0	3·15	
2 O	16·0	3·61	
3 Cl	106·5	32·02	
Au	199·0	44·34	44·54
	410·5	100·00	

According to these analyses, sincaline contains:

$$C_{10}\,H_{15}\,NO_3 = C_{10}\,H_{14}\,NO_2,\,HO.$$

It is, therefore, an oxygenated alkaloid, and, from a general view of its properties, may be regarded as belonging to the fourth class of

the alkaloids discovered by Hofmann, differing from these, however, in one circumstance—viz., that its gold- and platinum-salts contain oxygen.

SINAPINE.—The composition of sinapic acid and of sincaline affords a satisfactory explanation of the decomposition of sulphocyanide of sinapine by baryta-water. This decomposition is, in fact, expressed by the following equation:

$$\underbrace{C_{34}H_{25}N_2S_2O_{10}}_{\text{Sulphocyanide of Sinapine.}} + 3\,BaO = \underbrace{C_2NS_2Ba}_{\text{Sulphocyanide of Barium.}} + \underbrace{C_{10}H_{15}NO_3}_{\text{Sincaline.}} + \underbrace{C_{22}H_{10}O_8,\,2\,BaO}_{\text{Sinapate of Baryta.}}$$

It still, however, remains to be determined whether this body is to be regarded as the sinapate of a copulated base composed of sincaline and hydrosulphocyanic acid, like Fritzsche's cyanharmaline or Hofmann's cyaniline, or as the sulphocyanogen-compound of an alkaloid containing the elements of sincaline and sinapic acid. For the decision of this question, it is of great importance to know that there exist two modifications of sulphocyanide of sinapine, one of which reddens ferric salts immediately, like every other sulphocyanide, while the other does not produce that effect without the aid of heat. This circumstance explains the discrepancy existing in the statements of different authors respecting the so-called sinapine, some asserting that it reddens iron-salts, while others say that it does not.

The following reaction appears to throw still further light upon this question.

When a small quantity of strong sulphuric acid is added to a hot concentrated solution of sulphocyanide of sinapine in alcohol of 90 per cent, the liquid deposits, on cooling, a quantity of rectangular laminæ, which completely fill it. These crystals consist of the acid sulphate of a new alkaloid, to which the authors give the name of *Sinapine*, regarding it as the base of the sulphocyanide of sinapine. By filtration and washing with absolute alcohol, these crystals may be separated from the mother-liquor, which contains hydrosulphocyanic acid. Dried at 100°, they contain $C_{32}H_{26}NO_{12}$, $2\,SO_3$, as shown by the following analysis:

	Calculation.		Experiment.
32 C	192	47·06	46·99
26 H	26	6·37	6·37
N	14	3·43	—
12 O	96	23·53	—
$2\,SO_3$	80	19·61	19·82
$C_{32}H_{26}NO_{12}$, $2\,SO_3$	408	100·00	

The formation of this salt is represented by the following equation:

$$C_{34}H_{25}N_2S_2O_{10} + 2\,HO + 2\,SO_3 = C_{32}H_{26}NO_{12},\,2\,SO_3 + C_2NS_2H.$$

In the crystallized state, this acid salt likewise contains 4 atoms of water of crystallization, which it gives off at 110°. It has a strongly acid reaction, and dissolves readily in water and in boiling alcohol, from which it separates again on cooling.

All attempts to isolate the base in the solid state failed, in consequence of the facility with which it separates into sinapic acid and sincaline. But on adding baryta-water to a solution of the acid sulphate of sinapine, sulphate of baryta is precipitated, and the remaining solution, when freed from excess of baryta by careful addition of sulphuric acid, forms an intensely yellow liquid, having a distinctly alkaline reaction, and capable of precipitating many metallic oxides from their solutions. The solution, when evaporated, turns first green and then red, and leaves a non-crystalline residue, from which no definite compound is extracted, either by alcohol or by ether. When the solution of the acid sulphate is boiled with oxide of lead, the sinapine appears to form a compound with this base. On boiling the same solution with excess of potash or baryta, the sinapine is immediately resolved into sinapic acid and sincaline.

The salts of sinapine are colourless, and more stable than the base itself. The neutral sulphate is obtained by neutralizing the second equivalent of sulphuric acid in the acid sulphate with baryta-water, then filtering and evaporating. It forms a very soluble crystalline mass, from the solution of which the hydrochlorate or nitrate may be formed by careful addition of chloride of barium or nitrate of baryta. Both these salts crystallize in delicate, very soluble needles. On heating either of these salts with a solution of sulphocyanide of potassium, sulphocyanide of sinapine is reproduced, and crystallizes on cooling, exhibiting all the properties of the original substance.

From all these facts, we may conclude that the substance extracted from mustard is the sulphocyanide of a copulated base, the true *sinapine*, which is very unstable, and separates with the greatest facility into sinapic acid and sincaline.

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XVII.—*On the Amides.*

By C. Gerhardt.

(from a letter to dr. williamson.)

In my paper on the anhydrous acids, I have advanced the opinion that the majority of organic compounds hitherto well known may be derived from a very small number of types, belonging to mineral chemistry — such, for instance, as water, hydrochloric acid, ammonia, &c. Considered as terms of a series, the bodies derived from each of these types have not identical properties; their properties are, in fact, progressive, the difference between them increasing with the interval between the places in the series which they occupy. According to this view, we may comprehend under *one type*, acids, bases, and neutral bodies, the acids being placed at one end of the series, the bases at the other, and the neutral bodies which form the transition between the two extremes occupying the middle place. If, for the sake of simplification, we designate the two extremes by the words positive and negative, we may say that there are groups, or organic radicals, such as methyl, ethyl, phenyl, which being substituted for the hydrogen of the preceding types, produce *positive derivatives* —that is to say, bodies more or less resembling bases; whilst other groups or radicals, such as othyl* (or *acetyl*), benzoyl, cumyl, give rise, by a similar substitution, to *negative derivatives*, or bodies more or less

* The term "othyl" has been substituted for "acetyl" at the suggestion of Dr. Williamson, to avoid confusion between the oxygen-radical C_2H_3O and the hydrocarbon C_2H_3, to which the name of "acetyl" has long been applied.

analogous to acids. This point appears to me to be now completely established with regard to the derivatives of the water or oxide type, including the alcohols, ethers, hydrated acids and anhydrous acids; and it is no less evident in the derivatives of the hydrochloric acid type, comprising the chlorides which correspond to these different organic oxides.

With respect to the derivatives of the ammonia type, chemists, doubtless relying on the constancy of chemical characters exhibited by the derivatives of the same type, have regarded ammonia as the type of those bodies only which have strongly marked alkaline properties. In this point of view, the beautiful researches of Dr. Hofmann on the organic bases have enriched science with a considerable number of compounds. But these occupy only one extremity of the series—that is to say, the positive extremity, already occupied by alcohol and ether, or in general by those organic oxides which are similar to bases, and contain the same radicals as the alkaline ammonias themselves. But if, as I suppose, the properties of the derivatives of the same type, instead of being constant, vary in regular series, then there must also exist ammonias occupying the negative extremity of the series, together with the hydrated and anhydrous acids; in other words, the same groups or radicals which, by substitution for 1 or 2 atoms of hydrogen in water, give rise to hydrated or anhydrous acids, must also be able to take the place of 1, 2 or 3 atoms of hydrogen in ammonia, and thus produce neutral ammonias, and ammonias more or less acid. From this point of view, the already known amides of monobasic acids may, I think, be regarded as realizing the substitution of the first atom of hydrogen in ammonia by an acidifying group (benzoyl, othyl, cumyl); we know, in fact, that these amides are feeble acids, in which an atom of hydrogen may be replaced by mercury, silver, &c. But to complete the demonstration, it still remains to effect the same substitutions on the other 2 atoms of hydrogen in ammonia. This is, in fact, what M. Chiozza and myself have endeavoured to do, by the experiments which I proceed to describe.

At the commencement of this research an important point demanded our attention—namely, the preparation of the amides required for our experiments—preparations often lengthy and tedious when carried on by the usual processes. These we replace by a very simple and expeditious method, which consists in treating the solid commercial carbonate of ammonia directly with the chloride corresponding to the acid whose amide we wish to obtain. The action is immediate, carbonic acid is disengaged, and a simple washing with cold water dissolves

the chloride of ammonium formed in the reaction. In this manner, large quantities of benzamide, cuminamide, sulphophenylamide,* &c., may be obtained with the greatest ease. The negative chlorides required for these preparations are obtained by means of the perchloride or oxychloride of phosphorus. In place of the chlorides, the corresponding anhydrous acids may be used.

The amides thus produced, which we shall call *primary amides*, represent a molecule of ammonia in which 1 atom of hydrogen is replaced by the negative radicals, benzoyl, cumyl, othyl, salicyl, sulphophenyl, &c.

$$N\left\{\begin{matrix}C_7H_5O\\H\\H\end{matrix}\right.$$

Benzoylamide.

$$N\left\{\begin{matrix}C_7H_5O_2\\H\\H\end{matrix}\right.$$

Salicylamide.

$$N\left\{\begin{matrix}C_2H_3O\\H\\H\end{matrix}\right.$$

Othylamide.

$$N\left\{\begin{matrix}C_6H_5SO_2\\H\\H\end{matrix}\right.$$

Sulphophenylamide.

$$N\left\{\begin{matrix}C_{10}H_{11}O\\H\\H\end{matrix}\right.$$

Cumylamide.

To convert the preceding compounds into *secondary amides*, or amides representing a molecule of ammonia in which 2 atoms of hydrogen are replaced by the negative radicals, we heat these primary amides with an equivalent quantity of chloride of benzoyl, of cumyl, sulphophenyl, &c. Abundant fumes of hydrochloric acid are disengaged, and a residue is left consisting of the secondary amide. These operations must be conducted at a determinate temperature; for some primary amides, when heated too strongly, spontaneously suffer a secondary decomposition, resulting in the formation of nitriles (cyanides of the alcohol-radicals). This secondary decomposition often interferes considerably with the results of these experiments, and renders their execution much more difficult than would at first be supposed. The secondary amides may likewise be produced, in certain cases, by the action of the anhydrous acids on the primary amides.

With regard to the *tertiary amides*, representing a molecule of ammonia in which the 3 atoms of hydrogen are replaced by negative groups, their preparation is generally easier than that of the secondary amides; for these, having much more strongly marked acid properties than the primary amides, form metallic salts more easily, and these are acted upon, even in the cold, by the chlorides of benzoyl, cumyl, &c.

It is then by double decomposition that we produce our new

* The amide of Mitscherlich's sulphobenzidic acid.

amides—that is to say, by the same reaction which gives rise to the ethers, alkalies, and anhydrous acids.

Among the new compounds which we have already obtained, I may mention

Benzo-salicylamide . . . . . $N\begin{cases} C_7 H_5 O_2 \\ C_7 H_5 O. \\ H \end{cases}$

This substance crystallizes in extremely thin needles, insoluble in water, slightly soluble in alcohol, very soluble in the alkalies. Its alcoholic solution reddens litmus. It easily forms salts with silver, lead, copper, &c.

Cumo-salicylamide . . . . . $N\begin{cases} C_7 H_5 O_2 \\ C_{10} H_{11} O \\ H \end{cases}$

is similar to the preceding amide.

Benzo-sulphophenylamide . . . . . $N\begin{cases} C_6 H_5 SO_2 \\ C_7 H_5 O \\ H \end{cases}$

crystallizes in beautiful flattened needles, strongly acid, slightly soluble in water, easily soluble in alkalies. It easily forms salts, with bases.

The silver-salt, or

Argento-benzo-sulphophenylamide . . . . $N\begin{cases} C_6 H_5 SO_2 \\ C_{10} H_{11} O \\ Ag \end{cases}$

is obtained in beautiful colourless needles, soluble in boiling water.

Dibenzo-sulphophenylamide . . . . . $N\begin{cases} C_6 H_5 SO_2 \\ C_7 H_5 O \\ C_7 H_5 O \end{cases}$

crystallizes from ether in magnificent prisms, truncated with octohedral faces, and having a diamond-lustre. This compound bears the same relation to the preceding body that anhydrous benzoic acid bears to benzoate of silver, or to hydrated benzoic acid.

Cumo-benzo-sulphophenylamide . . . . . $N\begin{cases} C_6 H_5 SO_2 \\ C_7 H_5 O \\ C_{10} H_{11} O \end{cases}$

crystallizes in needles

Dibenzo-phenylamide (*Dibenzanilide*) . . . $N\begin{cases} C_6H_5 \\ C_7H_5O \\ C_7H_5O \end{cases}$

forms beautifully brilliant needles, slightly soluble in cold alcohol.

We are at present engaged in the study of the preceding bodies, and of many similar compounds. The number of the organic acids which form chlorides and anhydrous acids being very large, we may vary almost infinitely the substitutions by negative radicals, and thus form a vast number of new bodies. There is little doubt that many of the nitrogen-acids contained in plants exhibit a constitution similar to that of our new amides.

In a future communication I propose to speak of the *Diamides* (amides of bibasic acids), such as oxamide, of the *Acid Amides*, and the *Hydramides* (such as hydrobenzamide). The acid amides evidently correspond to the hydrated oxide of ammonium; they occupy one extremity of the series, at the other end of which are found the alkalies discovered by Dr. Hofmann (hydrated oxide of tetrethyl-ammonium), &c.

XVIII.—*On an Improved Apparatus for the Analysis of Gases.*

By Dr. E. Frankland, F.R.S. and W. J. Ward, Esq.

Notwithstanding the acknowledged importance of the investigation of gaseous bodies, it is only within a comparatively recent period that this branch of chemical research has received that attention which it so well deserves.

When Bunsen, in the prosecution of his admirable researches on the gases evolved from the iron-furnaces of Germany,* attempted to apply to the analysis of those gases the best methods known at that time, he found himself compelled, by the great imperfections and inaccuracies of those methods, to re-investigate and remodel the whole subject of gaseous analysis. Commencing with the construction of the eudiometers themselves, and adopting the simple plan of graduation independent of volume, with subsequent calibration or determination of the actual value of each division of this independent graduation, he attained a degree of accuracy in the measurement of volumes which left nothing to be desired in this department. He then obviated the

* Pogg. Ann. Bd. XLVI, 193; L, 81, 673.

inaccuracies inseparable from the introduction of liquid solvents into the measuring-tubes, by the employment of those solvents or absorbents in the dry state, in the form of little bullets cast upon platinum or steel wires. Thus the inner walls of the eudiometers were preserved free from adhering impurity, whilst the convexity of the internal mercury was kept uniform. By further improvements in the absorbents employed, the determination of the limits of perfect combustion in the explosion of gases with oxygen and hydrogen, and many other important points connected with the true measurement of gaseous volumes, Bunsen brought this branch of chemical analysis to a state of perfection which, as shown by numerous researches made by himself, by Playfair, Kolbe, and others, left, so far as delicacy and perfect accuracy were concerned, scarcely either room or desire for further improvement.

It was however necessary, for the successful carrying out of these methods, that a room of tolerably constant temperature should be appropriated exclusively to this object, and that an interval of from half an hour to one hour should be allowed between each determination of volume in order that the gas in the eudiometer might perfectly assume the temperature of the circumambient air. These circumstances, though of little importance in the performance of occasional gas analyses, become serious considerations when a large number of such analyses have to be made consecutively, as the expenditure of time and space becomes in such cases very great.

For the removal of this difficulty we are indebted to Regnault, who, by enclosing the eudiometer in a cylinder filled with water, renders the equalization of the temperature of the gas and the external medium, the work of a few seconds only; thus greatly reducing the time occupied by an analysis, and obviating the necessity for an apartment exclusively appropriated to gaseous investigations. This chemist has also further facilitated the various operations upon gaseous mixtures, by a more convenient division of the apparatus into two parts, the one for absorption and the other for measurement, than that employed by Bunsen; as also by adopting the admirable method of always determining the gaseous volumes when saturated with aqueous vapour. Unfortunately, these great advantages are in some respects diminished by a somewhat less amount of delicacy in the manner of determining the volumes: M. Regnault maintains the volume of the gases during an analysis, constant, and measures the amount of pressure exercised by that constant volume, over or under the pressure of the atmosphere, expressed in millimetres of mercury. This method, though unexceptionable in principle, has yet the dis-

advantage in practice, that considerable changes of volume are represented by small numerical expressions when compared with those obtained by Bunsen's method. This is more especially the case with the first determination in an analysis, great delicacy in which is usually of much greater importance than in the subsequent readings.

To illustrate more clearly what we here mean, we give the determination of a small percentage of carbonic acid, contained in a small volume of gas, by the two methods:

BY BUNSEN'S METHOD.

	Absorbed volume.	Temp.	Difference of mercury level.	Height of barometer.	Corrected vol. at 0^0 C. and 1^m pressure.
Vol. of gas used (dry)	330·2	0^0 C.	$550{\cdot}4^{mm}$	$760{\cdot}0^{mm}$	69·20
Vol. after absorption of CO_2 (dry) . .	327·8	0^0 „	549·6 „	760·1 „	69·00

BY REGNAULT'S METHOD.

	Observed pressure.	Temp.	Barometer.	Corrected pressure.
Gas used (moist) . .	—686·2	0^0 C.	$760{\cdot}0^{mm}$	69·2
After absorption of CO_2 (moist)	—686·5	0^0 „	760·1 „	69·0

Percentage of carbonic acid = 0·28.

Let us now suppose that an error of $\frac{1}{10}$ of a millimetre was made in the first observation in each of the above methods, and that thus the volume of gas used was read off according to Bunsen's method 330·1 vols., and according to Regnault's method — 686·3. The percentage of carbonic acid by the two methods would then be as follows:

Carbonic acid per cent (Bunsen's method) . . . 0·260
„ „ „ (Regnault's method) . . 0·145

Thus the error in the one case would amount to only ·02 per cent, whilst in the other it would be nearly 7 times as great, and might even cause the carbonic acid to be entirely overlooked.

In endeavouring to remedy this defect, and at the same time to combine the advantages of the two methods, we proposed to ourselves the following qualifications as highly desirable in a good apparatus for the analysis of gases.

1. The determinations of the gaseous volumes should be made in a manner entirely independent of the pressure and temperature of the external atmosphere.

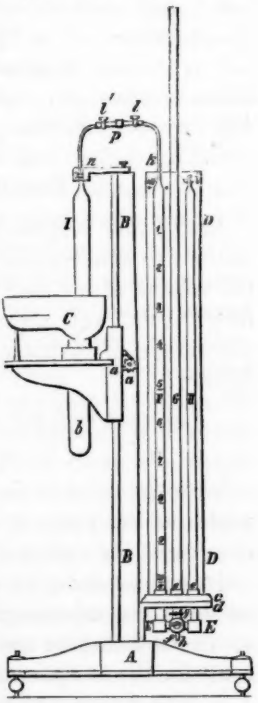
2. Such determinations of volume should also be self-correcting as

regards the tension of aqueous vapour and the variations in the density of mercury.

3. Each change of volume should be expressed by a numerical difference as large as possible.

4. In order to avoid the inconvenience and loss of time occasioned by tedious calculations, references to tables, &c., the numerical expression of each volume actually read off should either be the true and corrected volume, or a number from which such volume can be at once obtained by the most simple arithmetical process.

The advantage of securing the first and second of these qualifications is sufficiently obvious; for whilst we can then carry on the operations of gaseous analysis without an apartment of nearly constant temperature set apart for the purpose, the accuracy of our results is also not liable to be affected by any errors that may have been made in the determination of the expansion of gases by heat, the tension of aqueous vapour, and the expansion-coefficient of mercury. The third and fourth qualifications are also scarcely of inferior importance, the one for securing delicacy in the readings, and the other for economizing time and enabling the operator to see the corrected results of his experiments during their progress, an advantage which can be best appreciated by those who have had to make large numbers of consecutive gas analyses.



In constructing an apparatus to combine the foregoing qualifications, we have taken as a model the ingenious and very convenient arrangement of MM. Regnault and Reiset, with the mechanical arrangements of which, our apparatus, though different in principle, has much in common.

Our instrument, which is represented by the accompanying figure consists of the tripod *A* furnished with the usual levelling screws, and carrying the vertical pillar *B B*, to which is attached, on the one side, the moveable mercury-trough *C*,* with its rack and pinion *a a*, and on the other the glass cylinder *D D* with its contents. This cylinder is 36 inches long and

* The mercury-trough, including its tubular well *b*, may be conveniently constructed of gutta-percha.

4 inches internal diameter; its lower extremity is firmly cemented into an iron collar *c*, the under surface of which can be screwed perfectly water-tight upon the bracket-plate *d* by the interposition of a vulcanized caoutchouc ring. The circular iron plate *d* is perforated with three apertures, into which the caps *e e e* are screwed, and which communicate below the plate with the T-piece *E E*. This latter is furnished with a double-way cock *f* and a single-way cock *g*, by means of which the tubes cemented into the sockets *e e e* can be made to communicate with each other or with the exit-pipe *h* at pleasure.

F G H are three glass tubes, which are firmly cemented into the caps *e e e*. *F* and *H*, which are only slightly shorter than the glass cylinder, are each from 15^{mm} to 20^{mm} internal diameter, and are selected of as nearly the same bore as possible, to avoid a difference of capillary action. The tube *G* is somewhat wider, and may be continued to any convenient height above the cylinder. *H* is accurately graduated with a millimetre scale, and is furnished at top with a small funnel *i*, into the neck of which a glass stopper, about 2^{mm} in diameter, is carefully ground. The tube *F* terminates at its upper extremity in the capillary-tube *k*, which is carefully cemented into the small steel stop-cock *l*. *F* has also fused into it at *m* two platinum-wires for the passage of the electric spark. After this tube has been firmly cemented into the cap *e*, its internal volume is accurately divided into ten perfectly equal parts, which is effected without difficulty by first filling it with mercury from the supply-tube *G*, up to its junction with the capillary attachment, and then allowing the mercury to run off through the nozzle *h* until the highest point of its convex surface stands at the division 10, previously made so as exactly to coincide with the zero of the millimetre scale on *H;* the weight of the mercury thus run off is carefully determined, and the tube is again filled as before and divided into ten equal parts, by allowing the mercury to run off in successive tenths of the entire weight, and marking the height of the convexity after each abstraction of metal. By using the proper precautions with regard to temperature, &c., an exceedingly accurate calibration can, in this way, be accomplished.

The absorption-tube *I* is supported by the clamp *n*, and connected with the capillary-tube *k* by the stop-cock and junction-piece *l' p* in exactly the same manner as in Regnault's apparatus.

When the instrument is thus far complete, it is requisite to ascertain the height of each of the nine upper divisons on the tube above the lowest or tenth division. This is very accurately effected

in a few minutes by carefully levelling the instrument, filling the tube *G* with mercury, opening the cock *l* and the stoppered funnel *i*, and placing the cock *f* in such a position as to cause the tubes *F H* to communicate with the supply-tube *G*. On now slightly turning the cock *g*, the mercury will slowly rise in each of the tubes *F* and *H;* when its convex surface exactly coincides with the ninth division on *F*, the influx of metal is stopped, and its height in *H* accurately observed; as the tenth division on *F* corresponds with the zero of the scale upon *H*, it is obvious that the number thus read off is the height of the ninth division above that zero-point. A similar observation for each of the other divisions upon *F* completes the instrument.

Before using the apparatus, the large cylinder *D D* is filled with water, and the internal walls of the tubes *F* and *H* are once for all moistened with distilled water by the introduction of a few drops into each, through the stop-cock *l* and the stoppered funnel *i*. The three tubes being then placed in communication with each other, mercury is poured into *G* until it rises into the cup *i*, the stopper of which is then firmly closed. When the mercury begins to flow from *l*, that cock is also closed. The tubes *F* and *H* are now apparently filled with mercury, but a minute and imperceptible film of air still exists between the metal and glass; this is effectually got rid of by connecting *F* and *H* with the exit-tube *h* and allowing the mercury to flow out until a vacuum of several inches in length has been produced in both tubes; on allowing the instrument to remain thus for an hour, the whole of the film of air above mentioned will diffuse itself into the vacuum, and will become visible as a minute bubble in each tube on allowing the vacuum to be filled up from the supply-tube *G*. These bubbles are of course easily expelled on momentarily opening the cock *l* and the stopper *i* whilst *G* is full of mercury. The absorption-tube *I* being then filled with quicksilver, and attached to *l* by the screw clamp, the instrument is ready for use.

In localities where a constant supply of water from street mains can be had, the temperature of the water in the cylinder *D D* can be maintained perfectly constant by allowing a continuous stream, direct from the main, to flow into the bottom of the cylinder and make its exit near the top. By this arrangement, it has been proved by one of us, in an extensive series of experiments, that the temperature of a cylinder supplied from the Manchester high-pressure mains does not vary more than 0·02° C. in twelve hours, a variation which scarcely requires correction in the most delicate experiments.

In illustration of the manner of using our apparatus, we will take

as an example an analysis of atmospheric air. A few cubic inches of air freed from carbonic acid having been introduced into the tube *I*, it is transferred into *F* for measurement by opening the cocks *l l'* and placing the tube *F* in communication with the exit-pipe *h*; the transference can be assisted, if needful, by elevating the trough *C*. When the air, followed by a few drops of mercury, has passed completely into *F*, the cock *l* is shut, and *f* turned so as to connect *F* and *H* with *h*. Mercury is allowed to flow out until a vacuum of 2 or 3 inches in length is formed in *H*, and the metal in *F* is just below one of the divisions: the cock *f* is then reversed, and mercury very gradually admitted from *G* until the highest point in *F* exactly corresponds with one of the divisions upon that tube; we will assume it to be the sixth division. This adjustment of mercury and the subsequent readings can be very accurately made by means of a small horizontal telescope placed at a distance of about 6 feet from the cylinder, and sliding upon a vertical rod. The height of the mercury in *H* must now be accurately determined, and if from the number thus read off, the height of the sixth division above the zero of the scale on *H*, be deducted, the remainder will express the true volume of the gas; but in order to compare this with subsequent readings made at other divisions upon *F*, the number thus obtained, which evidently represents the pressure of the gas, is reduced to what it would have been had the gas been expanded to the tenth division of *F*. Bearing in mind that the pressure of a gas is inversely as its volume, this reduction is very simply effected by multiplying the number as above obtained by $\frac{6}{10}$, or 0·6; and in all cases, any determination of pressure made at any division upon *F* may be reduced to the pressure of the same volume when expanded to the tenth division, by the use of a fractional multiplier whose denominator is 10, and numerator the number of the division at which the determination is made.

As the temperature is maintained constant during the entire analysis, no correction on that score has to be made; the atmospheric pressure being altogether excluded from exerting any influence upon the volumes or pressures, no barometrical observations are requisite, and as the tension of aqueous vapour in *F* is exactly balanced by that in *H*, the instrument is in this respect self-correcting.

Hydrogen being then introduced in the same way as the original gas, and the volume determined anew, the electric spark is passed through the mixture by means of the platinum-wires at *m*, and the determination of the contraction caused by the explosion terminates the analysis. The following are the results of an analysis of air made in this way.

VOLUME OF AIR USED.

(Determined at fifth division on *F*.)

Observed height of mercury in *H*	. .	673·0^{mm}
Height of fifth division above zero	. .	383·0
Corrected pressure of gas . . .	=	290·0
		·5
Corrected pressure of gas at tenth division	=	145·00

VOLUME AFTER ADMISSION OF HYDROGEN.

(Determined at sixth division.)

Observed height of mercury in *H*	. .	772·3^{mm}
Height of sixth division above zero	. .	304·0
Corrected pressure of gas . . .	=	468·3
		·6
Corrected pressure of gas at tenth division	=	280·98

VOLUME AFTER EXPLOSION.

(Determined at fifth division.)

Observed height of mercury in *H*.	. .	763·3^{mm}
Height of fifth division above zero	. .	383·0
Corrected pressure of gas . . .	=	380·3
		·5
Corrected pressure of gas at tenth division	=	190·15

RESULTS.

Volume of air used . . .	145·00
Volume of oxygen . . .	30·276

Hence:

Nitrogen . . .	79·120
Oxygen . . .	20·880
	100·000

To show the delicacy of the indications of this instrument, we here subjoin the results of a series of analyses performed upon the same

specimen of atmospheric air, previously freed from carbonic acid by caustic potash.

	I.	II.	III.	IV.	V.	VI.
Oxygen	20·880	20·888	20·883	20·867	20·868	20·876
Nitrogen	79·120	79·112	79·117	79·133	79·132	79·124
	100·000	100·000	100·000	100·000	100·000	100·000

XIX.—*On the use of Hydrogen in determining Vapour-Densities, and on the Acidification of Alcohols by Oxygen-gas or Atmospheric Air.*

By Robert Railton.

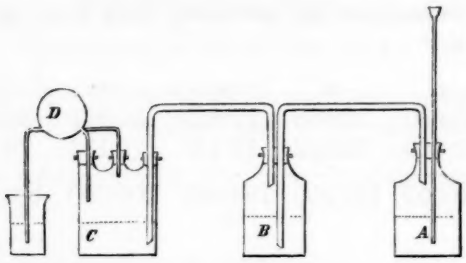
(of university college.)

Whilst engaged in some experiments on the alcohol obtained by M. Bouis from castor-oil, which by combustion I had already found to agree with the formula $C_{14}H_{16}O_2$, I had occasion to ascertain the density of its vapour.

On determining it by the usual method, I found that the experimental density greatly exceeded the calculated density, and that the condensed vapour had an acid reaction, although the liquid which was introduced into the glass globe was perfectly neutral. The latter circumstance led me to suppose that the vapour of the alcohol combined, at a high temperature, with the oxygen of the air contained in the globe, forming an acid vapour which would necessarily be heavier than the alcoholic vapour; indeed it would appear from the density I obtained (4·535) that the œnanthylic alcohol was wholly converted by oxidation into the corresponding acid, $C_{14}H_{14}O_4$, the theoretical density of which is 4·531. Subsequent experiments confirmed the supposition.

To decide the matter completely, Dr. Williamson suggested to me to substitute dry hydrogen for common air in the globe; this method was tried, and led to the most satisfactory results. The experiment was conducted as follows:

The globe was first weighed, full of dry air, and the requisite amount of alcohol afterwards introduced; the air was then displaced by diffusion, an apparatus, of which the following is the sectional sketch, being used.



In the bottle *A* the hydrogen is generated, whence it passes into the wash-bottle *B*, and thence into the bottle *C*; the two latter bottles contain concentrated sulphuric acid, which is intended to dry the hydrogen thoroughly.

The globe or vapour-flask is fixed, with its long narrow neck downwards, into one of the necks of the bottle *C* by an air-tight cork, the orifice of the neck of the globe being above the sulphuric acid.

The third neck of the bottle *C* is closed by a cork, which is traversed by a bent tube of fine bore, in order that the hydrogen and air may escape under some pressure; and as a precaution against the possible return of moist air into *C*, the outer end of this tube dips into concentrated sulphuric acid.

The evolution of hydrogen is continued for two or three hours, during which time the air is gradually expelled from the globe: the rest of the operation is the same as in taking ordinary vapour-densities.

The following are the results of two experiments—the first, when the globe contained atmospheric air; the second, when the above-described method was adopted:

FIRST EXPERIMENT.

Capacity of the globe at 60° F.	27·70 cub. in.
Weight of globe filled with air at 58° F. and 30·12 in. bar.	866·58 grs.
Weight of globe filled with vapour at 531° F. and 30·12 in. bar.	878·17 „
Volume of residual air at 57° F. and 29·73 in. bar.	·55 cub. in.
27·70 cub. in. air at 58° F. and 30·12 in. bar. become at 60° F. and 30 in. bar. 27·92 cub. in., and weigh	8·66 grs.
Hence, weight of empty globe is . . .	857·92 „

The capacity of the globe at 531° F. . . .	27·87 cub. in.
Volume of residual air at 531° F. . . .	1·06 „
Volume of vapour at 531° F. and 30·12 in. bar. .	26·81 „
which at 60° F. and 30 in. bar. become . .	14·59 „
Weight of residual air	·17 grs.
„ empty globe	857·92 „
	858·09 „
Weight of globe and vapour	878·17 „
Weight of 14·59 cub. in. vapour at 60° F. . .	20·08 „
Weight of 100 cub. in. vapour	137·63 „
Whence the experimental density is . . .	4·535
Calculated density of the acid $C_{14} H_{14} O_4$ . .	4·531
Calculated density of the alcohol $C_{14} H_{16} O_2$.	4·018

SECOND EXPERIMENT.

Capacity of globe at 60° F.	24·50 cub. in.
Weight of globe filled with air at 56° F. and 29·65 in. bar.	1577·077 grs.
Weight of globe filled with vapour at 552° F. and 29·65 in. bar.	1584·876 „
Residual hydrogen at 60° F.	·20 cub. in.
24·50 cub. in. of air at 56° F. and 29·65 in. bar. become at 60° F. and 30 in. bar. 24·4 cub. in., and weigh	7·566 grs.
Hence, weight of empty globe	1569·511 „
Capacity of globe at 552° F.	24·67 cub. in.
Volume of residual hydrogen at 552° F. . .	·39 „
Volume of vapour at 552° F. and 29·65 in. bar.	24·28 „
which at 60° F. and 30 in. bar. become . .	12·323 „
Weight of residual hydrogen	·008 grs.
Weight of empty globe	1569·511 „
Weight of globe and vapour	1569·519 „
	1584·876 „

Weight of 12·323 cub. in. vapour at 60° F. .	15·357	grs.
Weight of 100 cub. in. vapour	124·62	„
The experimental density is therefore . . .	4·019	
The theoretical density of the alcohol $C_{14} H_{16} O_2$ is	4·018	

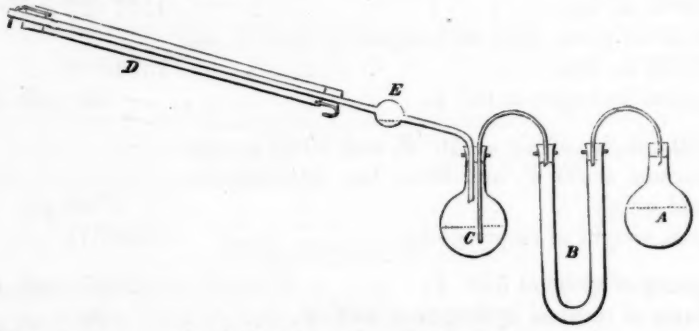
I may here remark that the condensed vapour in the last experiment was perfectly neutral.

These results suggested the idea that it was possible to convert the alcohol $C_{14} H_{16} O_2$ into the corresponding acid $C_{14} H_{14} O_4$ by simply passing a stream of dry oxygen or atmospheric air into the liquid while heat was being applied to it. To test this idea, an apparatus of the following construction was adopted:

A is a flask containing chlorate of potash and binoxide of manganese. *B* is a tube containing chloride of calcium or other desiccating substance.

The alcohol to be oxidized is placed in the flask *C*. *D* is an arrangement of glass tubes forming a Liebig's condenser; *E* is a bulb blown on the inner glass tube of the arrangement *D*.

The construction will be understood on referring to the figure, which is drawn in section.



The alcohol in the flask *C* is made to boil briskly; at the same time, oxygen is supplied from *A* (or from a gas-holder); the oxygen enters at the bottom of the liquid. The vapour from *C* is condensed by the arrangement *D*, and continually flows back into *C*, until the whole is fully oxidized; but as, during the process, water is formed, and as it would endanger the safety of the flask *C* if allowed to re-enter it, the bulb *E* is interposed, when the water, being of greater density, collects at the bottom of *E*, and the oily liquid alone returns to the flask *C*, there to undergo the same operation as before, until it is completely oxidized.

A considerable quantity of œnanthylic acid was obtained by this process, from which the baryta- and potash-salts were formed.

Fusel-oil was also oxidized in a similar manner, and doubtless the whole of the alcohols would yield their corresponding acids if subjected to the same treatment.

This subject was not further proceeded with, as my success in these experiments induced me to try others of contrary character, in which I am at present engaged. If they succeed—and there is some reason to believe they will—we shall have it in our power to produce artificially all the alcohols from their corresponding acids, by an extremely cheap and simple process. The deoxidation will be effected by hydrogen.

Whatever the results of my present experiments may be, as soon as they are completed, I shall have the honour of communicating them to the Society.

XX.—*On the use of Gas as Fuel in Organic Analysis.*

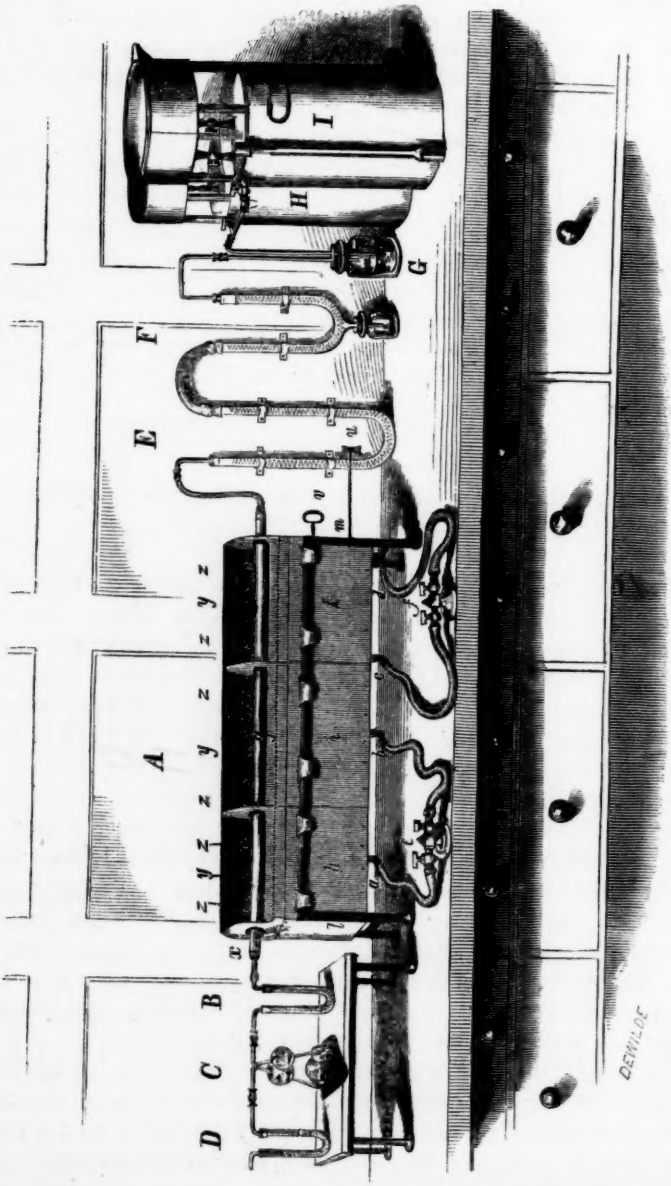
By A. W. Hofmann, Ph.D., F.R.S.

The extensive and daily increasing application of gas as a source of heat in the laboratory, naturally suggested the idea of using this convenient fuel likewise in organic analysis. A variety of arrangements have been proposed for this purpose, but not one of them has as yet come into general use. The difficulties which present themselves are, in the first place, the production of a sufficiently high temperature; and secondly, the regulation of the heat according to the special requirement of the process. In order to accomplish the analysis at the temperature of an ordinary air-flame, it has been found necessary to abandon the simple process of Liebig, and to have recourse to the more complicated method of completing the combustion in an atmosphere of oxygen; on the other hand, in order to obtain a sufficient control over the temperature, an arrangement has been devised, which may appear intricate at the first glance, but which works with sufficient facility and precision, although it may hereafter probably be simplified.

The general disposition of the apparatus differs but little from the arrangement used in performing the combustion in oxygen-gas by means of spirits of wine, and is sufficiently intelligible by a glance at Fig. 1.* *A* is the combustion-furnace, which is supplied with gas by

* The wood engravings are taken from Liebig's "Handbook of Organic Analysis," edited by A. W. Hofmann. London, Walton and Maberly, 1853.

FIG. 1.



the tubes *a b c d*, communicating with two pairs of stopcocks, *e* and *f*; a combustion-tube, *g*, open at both extremities and supported in the

usual manner, communicates in front with the chloride-of-calcium-tube *B*, a potash-bulb-apparatus *C*, and a potash-tube *D*; at the back, the combustion-tube communicates by means of a system of desiccators, consisting of a potash-tube *E*, a sulphuric-acid-tube *F*, and a sulphuric-acid-bottle *G*, with the gas-holders *H* and *I*, containing respectively oxygen and atmospheric air. The bottle *G* serves, moreover, as a bubble-gauge for measuring the rapidity of the current.

The furnace consists of three separate compartments of strong iron plate *h i* and *k*, which are supported by a stout iron stand *l m*. The arrangement of these compartments requires a few explanations; their construction is evident from Figs. 2 and 3; *h* and *i* are simply

FIG. 2.

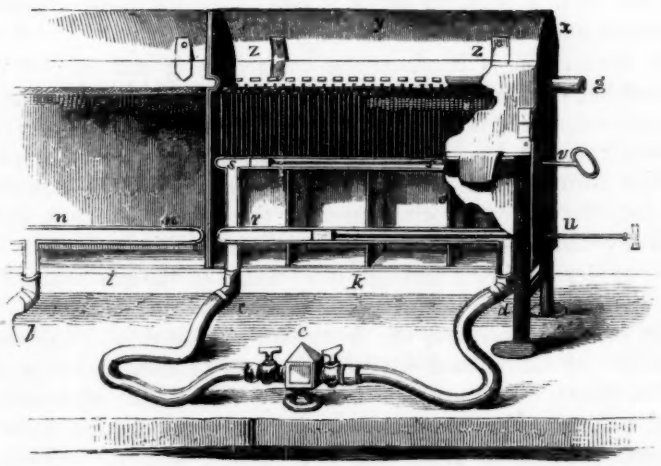
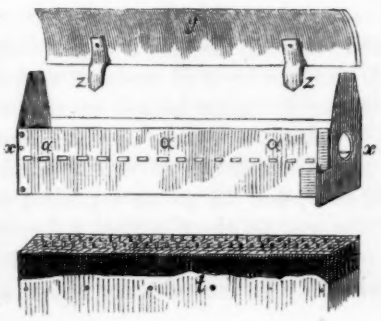


FIG. 3.



rectangular iron boxes, open at the bottom and covered at the top, with wire-gauze, which are supplied by horizontal perforated gas-pipes (*n n*, Fig. 2). The last compartment *k* (Fig. 2) has a somewhat more complicated construction. It differs from the two others by being subdivided into four smaller chambers by the three diaphragms, *o*, *p* and *q*, of iron plate, the gas being supplied by

two pipes instead of one. The lower pipe *r r* resembles in every respect the gas-pipe *n n* of the other compartments. The upper pipe *s s*, on the other hand, supplies the gas to two rows of vertical fine tubes, somewhat similar to those used in Leslie's gas-burner, the extremities of which project through the wire-gauze cover of the compartment (Fig. 3). Both pipes are provided with air-tight pistons, which enable the operator to manage the heat produced by this part of the apparatus according to the requirements of the analysis. Fig. 3 shows the manner in which the frame *x* which supports the combustion-tube is fitted over the wire-gauze cover of the case. It is provided with a series of holes *a*, allowing a current of air to enter, which bends the flame round the combustion-tube; this figure gives, moreover, a separate view of one of the side-pieces *y*, which by means of the tongues *z* are fastened upon the frame, in order to form a kind of dome, from which the heat is reflected downwards upon the combustion-tube.

The combustion is conducted in the following manner: A combustion-tube, open at both ends, and 2 or 3 inches longer than the combustion-furnace, is filled with a layer of oxide of copper, corresponding to the length of the two compartments *h* and *i*, placed into the furnace and connected at one end with the desiccators *E F*, &c., the other end being open at the time. The tube is then heated by the air-flame of the three compartments, and a slow current of dry air forced through it by means of the gas-holder *I*, for about five minutes, which removes every trace of moisture. The current being interrupted, the front end is corked, and the supply of gas so far diminished in compartments *h* and *i* that a mere sheet of flame remains upon the wire-gauze, whilst it is entirely turned off from the compartment *k*. As soon as the tube has sufficiently cooled, the front end is connected with the chloride-of-calcium-tube *B*, the potash-bulbs *C*, and the potash-tube *D*, and a little platinum boat containing the substance to be analyzed, introduced at the other extremity, and pushed in about two-thirds of the division *k*. All joints being well secured, the gas is again fully supplied to compartments *h* and *i*, and the layer of oxide of copper corresponding to the length of these divisions heated to a dull redness. The distillation of the "substance" may now be commenced. For this purpose, the gas is admitted, by means of the flexible tube *d*, to the lower gas-pipe *r r*, and the piston *u* pushed so far from the inlet as to supply the gas to the chamber *o l* only, whilst it is excluded from the other chambers, Fig. 2. In this manner, an air-flame is obtained which keeps the posterior extremity

of the combustion-tube at a dull red heat. A small quantity of gas is next admitted to the upper gas-pipe *s s*, by means of the flexible tube *c*, the piston *r* being drawn so far from the inlet as to confine the gas to a very few of the little tubes, at the extremity of which mere points of flame are thus produced. The distillation now proceeds with perfect regularity, the slow air-current, which must be kept up all the while, as well as the high temperature of the posterior portion of the tube, driving all the products of combustion towards the red-hot oxide of copper, which effects their perfect combustion. The piston *v* is gradually drawn out, so as to bring all the jets into play, and the supply of gas to the jets increased as far as possible without producing too smoky a flame. As soon as the temperature of the jets is no longer capable of expelling volatile matter from the substance, the piston *u* of the lower tube is gradually pushed in, and the gas supplied to all the chambers of compartment *k*, until the whole of the combustion-tube is exposed to an uniform air-flame throughout its whole length. A new quantity of matter is thus expelled, but unless the substance under examination be volatile, a large quantity of carbon is left in the boat.

At this period the air-current is replaced by a slow stream of oxygen from the gas-holder *H*, the arrival of which in the combustion-tube is marked by a brilliant phenomenon of incandescence. After a few minutes, the boat is left clean, and the combustion is terminated. The current is, however, kept up for a very short time longer, and stopped only when pure oxygen may be traced at the mouth of the potash-tube by means of an ignited splint of wood.

By this time the products of combustion are perfectly swept from the tube, and lodged in their receptacles; moreover, the copper is completely re-oxidized; the flame is now gradually lowered, and the gas at last entirely turned off; and if the combustion-tube, after the detachment of the chloride-of-calcium-tube, &c., and the removal of the empty platinum boat be carefully corked, the whole arrangement is ready for another combustion, in which the operation of drying, of course, becomes unnecessary.

Liquids may be likewise burned with the apparatus; in fact, on account of the facility with which the temperature of the compartment *k* can be managed, this mode of proceeding is particularly adapted to liquids. Even very volatile liquids, such as ether, &c., may be safely burned; in this case the combustion can be completed without any oxygen, and no fear of an explosion need be entertained.

In the case of substances containing nitrogen, the copper turnings

perfectly dried in a current of hydrogen, must be placed into the combustion-tube, *after* the preliminary desiccation, and the current of air must be very slow; it is, moreover, advisable to place some copper-turnings behind the boat with the substance, over the posterior compartment; the copper is thus heated to redness, and deprives the air-current of the greater part of its oxygen.

The first putting together of this apparatus requires considerable time, and the securing of so many joints is attended with some difficulty; but once fitted up, it enables the operator to analyze with great dispatch, scarcely more than an hour being necessary for making a complete combustion. The arrangement is particularly useful when a considerable number of analyses have to be made. There are, moreover, several additional advantages which deserve to be noticed. The determinations, both of carbon and hydrogen, are very exact, especially the latter, all sources of accidental moisture being excluded. On this account it is possible to reduce the amount of substance used in the analysis to a minimum, not more than from 150 to 200 milligrs. being required. The possibility of determining the amount of ash or the quantity of silver, platinum or barium, &c., in a substance, together with the carbon and hydrogen, is likewise frequently a very great convenience. The number of accidents is, moreover, much smaller. The combustion-tubes very rarely crack if the application of heat be sufficiently gradual. For this purpose it has been found convenient to light the gas in the commencement, below the wire-gauze, until the furnace has become hot, then to turn it off and to light it above the wire-gauze. But if an accident actually take place with a combustion-tube, it almost invariably occurs in the preliminary heating of the oxide of copper, and in such cases the "substance" is perfectly safe, and has only to be shifted to another tube. The combustion-tubes usually stand six or eight combustions, but frequently as many as ten or twelve may be made with the same tube, so that there is also a considerable saving in expense.

The only inconvenience incident to the apparatus is, that it is liable to get out of order. The wire-gauze especially has to be often renewed, and on this account a construction has been selected, which renders it possible to replace the wire-gauze in the laboratory, without sending the furnace to a gas-fitter.

The furnace given in the above illustrations is composed of three distinct divisions, which may be separately fixed upon the support. By this provision the apparatus becomes adapted to a variety of operations, especially to nitrogen-determinations, which require a shorter tube. This separation, however, is not absolutely necessary,

and for the special purpose of the carbon-, and hydrogen-determinations a furnace made in one piece answers equally well.

In conclusion, the results of several analyses performed by means of the above apparatus may be quoted.

Combustion of sugar:

I. 0·155 grm. of sugar gave
0·240 „ carbonic acid, and
0·092 „ water.
II. 0·3035 „ sugar gave
0·4685 „ carbonic acid, and
0·1765 „ water.
III. 0·226 „ sugar gave
0·3493 „ carbonic acid, and
0·1319 „ of water.

	I.	II.	III.	$C_{12}H_{11}O_{11}$
Carbon . .	42·16	42·09	42.17	42·10
Hydrogen .	6·59	6·46	6·48	6·43

Combustion of benzoic acid:

0·1695 grm. of benzoic acid gave
0·4275 „ carbonic acid, and
0·077 „ water.

		$C_{14}H_6O_4$
Carbon . . .	68·78	68·85
Hydrogen . .	5·04	4·91

Combustion of oil of turpentine:

0·1185 grm. of oil of turpentine gave
0·3842 „ carbonic acid, and
0·1240 „ water.

		$C_{10}H_8$
Carbon . . .	88·42	88·23
Hydrogen . .	11·62	11·77

Combustion of ether:

0·1561 grm. of ether gave
0·3695 „ carbonic acid, and
0·1915 „ water.

		$C_8H_{10}O_2$
Carbon . . .	64·55	64·86
Hydrogen . .	13·62	13·51

The preceding analyses were made by Mr. Charles Tookey for the especial purpose of testing the practicability of the gas-furnace. The following numbers are quoted from a paper shortly to be published by Messrs. Reginald Morley and John Abel:

Combustion of diethylotoluidine:

0·1495 grm. of diethylotoluidine gave
0·4435 „ carbonic acid, and
0·1410 „ water.

		$C_{22}H_{17}N$
Carbon	80·90	80·98
Hydrogen	10·47	10·43

Combustion of chloride of triethylo-toluammonium and bichloride of platinum:

0·530 grm. of salt gave
0·760 „ carbonic acid,
0·269 „ water, and
0·131 „ of platinum.

		$C_{26}H_{22}NCl, PtCl_2$
Carbon	39·10	39·24
Hydrogen	5·63	5·53
Platinum	24·71	24·90

An analysis of iodide of tetramethylammonium, likewise made by Mr. Tookey, gave the following results:

0·4138 grm. of iodide gave
0·3626 „ carbonic acid, and
0·2237 „ water.

		$C_8H_{12}NI$
Carbon	23·89	23·89
Hydrogen	6·00	5·97

XXI.—*On the Acetates and other Compounds of Alumina.**

By Walter Crum, F.R.S.,

PRESIDENT OF THE PHILOSOPHICAL SOCIETY OF GLASGOW.

The salt from which most of the products described in the present memoir were produced, is the tersulphate of alumina, now manu-

* Read before the Philosophical Society of Glasgow, April 27, 1853.

factured in large quantity in the north of England, under the name of concentrated alum. It is formed by the direct action of sulphuric acid upon clay, and, after a certain purification, is evaporated and sold in cakes.

The impurity which the commercial article contains in largest quantity is potash-alum. To separate that substance advantage was taken of its insolubility in a saturated solution of the tersulphate. The cake-alum was dissolved in a quantity of boiling water insufficient for its entire solution in the cold. On cooling, the excess of sulphate of alumina, mixed with almost the whole of the potash-alum, deposited, and was separated by filtration through calico. The filtered solution was then evaporated and cooled, when the tersulphate was found to crystallize in granular spongy masses. It was then drained and separated as much as possible from the mother-liquor by strong pressure between numerous folds of calico. The product was redissolved in boiling water, and again crystallized and pressed.

A salt was thus obtained, having little more than traces of the arsenious acid and the potash of the original material, together with a little iron and chloride of sodium. It has the formula

$$Al_2O_3, 3SO_3 + 18HO$$

first observed in 1825 by Boussingault in the hair-like substance found among the black schistus of the Andes of Columbia, near Bogota. He afterwards found the same substance in the volcano of Pasto, (north of Quito,) where it is formed by the action of the sulphurous vapours upon the schistus. It exists there in such quantities as to have enabled the Pastusos to become the manufacturers of chemical products for the whole country. They dissolve the alum in water, evaporate it to dryness, and form it into spherical masses like camphor, which are altogether free from iron.

The same substance is formed in this neighbourhood from a schistus containing pyrites, in which case it is mixed or combined with sulphate of iron.

The quantity of cake-alum now produced annually at Newcastle and at Sowerby-bridge, according to statistics furnished me by Mr. Wilson of Hurlet, is .	1,500	tons.
And of crystallized alum (chiefly ammoniacal) in England	13,200	„
Ditto ditto ditto in Scotland . .	4,200	„
Total in Great Britain . . .	18,900	tons.

It is estimated by Mr. Wilson that about one-fourth of this quantity

is consumed by calico-printers, and converted more or less completely into acetate of alumina. There is no other example of a substance so important and so extensively employed in the arts, as acetate of alumina, having been so little attended to by chemists.

INSOLUBLE ACETATES OF ALUMINA.

I. *Insoluble Binacetate of Alumina.* (5—*Hydrate*).—An acetate of alumina was produced by mixing together strong solutions of tersulphate of alumina (purified as already described) and of acetate of lead. They were poured slowly together into a vessel surrounded with cold water, and much agitated to reduce the temperature of the mixture. To the filtrate was added sulphide of hydrogen, to precipitate the lead of the sulphate of lead which remained in solution; and acetate of baryta to throw down its sulphuric acid.

The strongest solution formed in this way contained about 5 per cent of alumina, (from about 6 lbs. acetate of lead in an imperial gallon of the mixture).

When such a solution (or one containing even 4 per cent of alumina) is set aside and left at rest at a temperature of 60° or 70° Fahr., it begins after four or five days (without losing much of its transparency) to deposit upon the vessel a crust, which continues for some time to increase in thickness. When the liquid is poured off, and the crust allowed to dry, it separates readily from the vessel in hard plates like porcelain. If the solution be not left strictly at rest, it becomes turbid after some days, and the crust is produced in a more friable state. In cold weather the solution remains unaltered for a much longer time. Heated to redness, the salt becomes black from the decomposition of part of its acetic acid, and in this state it very slightly affects the colour of moistened litmus-paper, showing that it retains but little alkali. Dissolved in nitric acid and tested with nitrate of silver, it showed a trace of chlorine. It was freed entirely from these impurities by the process detailed in the succeeding chapter; still retaining, however, a trace of iron.

To ascertain the quantity of alumina in one of these salts, it is enough to moisten it with rectified and concentrated sulphuric acid in a platinum crucible, to evaporate the excess of acid over a spirit-lamp, and then to subject it to a white heat for half-an-hour in a furnace. The sulphuric acid expels acetic acid, and thereby secures the absence of charcoal. It facilitates the disengagement of water; and the powder, which, without it, becomes so pulverulent by calcination as to be with difficulty prevented from escaping, is thereby rendered coherent.

Attempts were first made to determine the acetic acid by the alkalimeter, taking potash-alum of known purity for a standard, and for a comparison of results. The substance being kept in water at a boiling-heat during the addition of the alkali, (soda,) and by a careful comparison of the shades of the litmus-paper, appeared at first to redden that test, so long as any portion of the salt remained undecomposed. But it was found, after some practice, that at least 5 per cent of the insoluble salt remained untouched by the alkali after all trace of acid reaction had disappeared in the process, and that within a range of 3 or 4 per cent the method was not to be depended upon. It gave valuable assistance, however, in this investigation, in the testing of solutions of alumina, with which it gave results much more accurate than with the insoluble salts.

33·24 grs. of the substance, dried first in the air, then pulverized and dried further in a stove twenty hours at 100° Fahr., were moistened with 80 grs. of rectified sulphuric acid in a platinum crucible, and calcined as above. There remained 8·64 grs. When this residue was treated with water and filtered, the solution showed no trace of sulphuric acid, and was alumina nearly pure=25·99 per cent of the original substance.

In another experiment, 32·64 grs., dried four hours in the stove, and treated as above, left 8·4 grs. of alumina=25·74 per cent. The mean is 25·86 per cent of alumina.

Burned with oxide of copper, 2·985 grs. produced 5·526 cub. inches of dry carbonic acid=2·612 grs., and corresponding to 50·69 per cent of acetic acid. In another experiment 1·685 grs. indicated 50·58 of acetic acid. The mean is 50·63. It was assumed that the remaining 23·51 per cent was water. The salt was therefore composed of—

Acetic acid . . .	50·63
Alumina	25·86
Water	23·51
	100·00

The formula, $Al_2O_3, 2\bar{A} + 5\,HO$, requires—

Acetic acid . . .	51·41
Alumina	25·91
Water	22·68
	100·00

II. *Insoluble Binacetate of Alumina.* (2—*Hydrate.*)—If heat

be applied to the strong solution of acetate of alumina, described in the previous pages, it speedily becomes turbid, and deposits a heavy white powder, which falls readily to the bottom of the vessel. In a couple of days, at 100° Fahr., a considerable quantity of this powder is deposited; but in two or three hours at 160°, and in much shorter time at boiling heat, the whole of the salt is thrown down, and nothing remains in the liquid but acetic acid, excepting a trace of alumina, just distinguishable by carbonate of soda.

The precipitate has a crystalline shining appearance in the moist state, and seems, under the microscope, to consist of small oval particles of uniform size. It falls into fine powder in drying, after which, when mixed with water, it remains for a long time in suspension. Boiling water does not free it from chloride of sodium, of which it contains about 0·1 per cent.

To remove that impurity, the substance is to be dissolved with the assistance of heat in 2 equivs. of rectified sulphuric acid, diluted with three times its weight of water. The solution is decomposed by subacetate of lead—

$$\mathrm{Al_2\,O_3,\,2\,\bar{A}+2\,SO_3+2\,PbO,\,\bar{A}}$$
$$\mathrm{=Al_2\,O_3,\,3\,\bar{A}+2\,(PbO,\,SO_3)}$$

and the filtrate freed from lead and sulphuric acid as before. When heat is now applied to this solution, a precipitate is obtained, in which no trace of alkali or of chlorine can be detected.

A portion of the substance obtained at a boiling heat, and dried twenty-four hours at 100° Fahr., yielded 29·83 per cent of alumina. Another portion dried forty-eight hours gave 30·54 per cent. Burned with oxide of copper, 1·697 grs. of the salt, dried at 100° Fahr., indicated 59·87 per cent of acetic acid. In another experiment 1·605 grs. indicated 58·88 per cent. The mean is 59·37. The substance is, therefore, composed of—

Acetic acid . . .	59·37
Alumina	30·18
Water	10·45
	100·00

The formula, $\mathrm{Al_2\,O_3,\,2\,\bar{A}+2\,HO}$, requires—

Acetic acid . . .	59·51
Alumina	29·99
Water	10·50
	100·00

Numerous specimens of this salt were formed by precipitation from solutions of various strengths, at various temperatures below boiling water, and analyzed for acetic acid and alumina. They generally agreed in the proportions of acid and base, but varied in the absolute quantity; indicating a range of from 3 to 5 equivs. in the proportions of water. The two salts which have been described as deposited, one at 60° and the other at a boiling heat, gave results nearly uniform.

When heat is applied to a solution of teracetate of alumina weaker than that which has been described, to one, for example, containing 3 per cent of alumina, it also yields the insoluble binacetate, but, in that case, not acetic acid alone, but a considerable quantity of acetate of alumina remains in the solution. Solutions containing 2 per cent of alumina are precipitated by boiling, if they have been kept some weeks, but not if recently prepared. It appears from these experiments, that the presence of free acetic acid favours, in some way, the production of the insoluble binacetate of alumina from a solution of teracetate. It was found, accordingly, that a solution of teracetate containing $\frac{3}{4}$ per cent of alumina, and which could not therefore be precipitated by boiling, acquired that property when made to contain acetic acid equal to a solution of teracetate with 4 per cent of alumina.

In whichever way deposited, this substance is exceedingly insoluble in water, either cold or hot, and it is equally insoluble in acetic acid. When 1 part of it is digested for an hour and a half in 200 parts of boiling water, it dissolves; and the solution consists partly of soluble binacetate of alumina, and partly of acetic acid and the bihydrate of alumina, to be afterwards described.

It dissolves in 2 equivs. of sulphuric acid, or of hydrochloric, or nitric acid, forming bisalts of alumina, and liberating the 2 atoms of acetic acid. It also dissolves in a strong solution of tersulphate of alumina, with the assistance of heat, forming bisulphate of alumina and free acetic acid.

$$2\,(Al_2\,O_3,\,3\,SO_3) + Al_2\,O_3,\,2\,\bar{A} = 3\,(Al_2\,O_3,\,2\,SO_3) + 2\,\bar{A}.$$

The mixture does not precipitate on the addition of water like the bisulphate alone, and must therefore be changed by water into tersulphate and binacetate of alumina.

$$2\,(Al_2\,O_3,\,3\,SO_3) + Al_2\,O_3,\,2\,\bar{A}.$$

A solution of potash-alum dissolved this binacetate in the same circumstances, but on the heat being continued for some time, a

precipitate was formed anew, which appeared from a qualitative analysis to be the monosulphate of alumina and potash,

$$KO,\ SO_3 + 3\ (Al_2,\ O_3,\ SO_3)$$

the substance which is formed when hydrate of alumina is boiled with alum. The same substance is found native, under the name of alum-stone, at La Tolfa, the seat of the celebrated manufacture of Roman alum, near Civita Vecchia; and was ascertained, by Collet Descotils, to be formed of—

$$KO,\ SO_3 + 3\ (Al_2\ O_3,\ SO_3) + 9\ HO.$$

SOLUBLE ACETATES OF ALUMINA.

Soluble Binacetate of Alumina. $Al_2\ O_3, 2\ \bar{A} + 4\ HO$.—Notwithstanding the tendency of a concentrated solution of the teracetate of alumina to deposit the insoluble salt, it may be evaporated, with certain precautions, to a dry substance soluble in water. For this purpose it must be spread very thin over sheets of glass, or of porcelain, exposed to a heat not exceeding 100° Fahr., and, as it runs together into drops, like water upon an oiled surface, it must be constantly rubbed with a thin platinum or silver knife. If these precautions are neglected, a mixture is obtained of the insoluble with a soluble acetate.

The soluble salt is thus produced in scales, having the appearance of gum when moistened, and leaving no residue when dissolved in water.

For analysis it was reduced to powder, and dried in the air twenty-four hours, at the temperature of 100° Fahr. The alkalimetric method was first employed, and it indicated 54·8 per cent of acetic acid; but the more accurate method, by oxide of copper, gave 55·82 per cent of acid. In experiments for the alumina 26·4 per cent was obtained. The composition of the substance was thus—

Acetic acid . . .	55·82
Alumina	26·40
Water	17·78
	100·00

But the solution from which this substance was obtained was a teracetate, and contained for the same quantity of alumina,

Acetic acid . . .	78·58

It lost, therefore, during gentle evaporation, nearly one-third of its

acetic acid, and was reduced almost to a binacetate, the formula of which—

$$Al_2O_3, 2\overline{A} + 4HO$$—requires—

Acetic acid . . .	52·38
Alumina	26·40
Water	18·49
	97·27

The excess of acetic acid = 3·44 per cent over the proportions of a binacetate, was presumed to be free acid adhering to the product. To remove that excess, a portion of it was heated in a water-bath, and afterwards treated with water. A considerable quantity of insoluble matter was left, and the solution on being evaporated to dryness, at a gentle heat, produced a soluble acetate, of which 100 parts contained—

Of acetic acid . . .	49·55
And of alumina . . .	32·47

corresponding, therefore, in composition, to a sesquiacetate; but it can only be looked upon as an accidental mixture, for every fresh portion that was produced in a similar way gave a different result—the amount of acid depending upon the extent and duration of the heat.

The binacetate of alumina may be produced at once in solution; and as it is the most suitable combination from which to form the dry soluble binacetate, as well as other bodies, I shall describe particularly the manner of obtaining it. Dissolve 24 parts of precipitated binacetate of alumina in 15 of rectified sulphuric acid, and 40 of water. Dilute further with 100 parts of water, and add carbonate of lead (about 44 parts) to precipitate the sulphuric acid.

$$Al_2O_3, 2\overline{A} + 2SO_3 + 2(PbO, CO_2)$$
$$= Al_2O_3, 2\overline{A} + 2(PbO, SO_3) + 2CO_2.$$

Filter the solution, and pass sulphide of hydrogen through it until it ceases to precipitate lead, and then add acetate of baryta, so long as it is precipitated by the sulphuric acid of the sulphate of lead which had remained in solution. When in this state, if the mixture be well agitated for half an hour in an open vessel, the excess of sulphide of hydrogen will be removed, and it may be filtered without the danger of the filtrate becoming afterwards milky. A solution of binacetate of alumina is thus obtained, containing about 4 per cent of

alumina, which is the strongest solution, even of the binacetate, that can be preserved for a length of time without depositing an insoluble salt.

Spread very thinly over a sheet of glass, it evaporates at 60° or at 100° Fahr., without running into large drops so much as the teracetate, and without having an equal tendency to produce the insoluble binacetate. The scales into which it forms in drying are transparent and soluble in water.

Burned with oxide of copper for acetic acid, and calcined for alumina, 100 parts were found to contain—

Acetic acid . . .	55·21
Alumina	31·31

But the alkalimeter had shown, that in the solution the same quantity of alumina had been combined with—

Acetic acid . . .	59·13

More than 4 per cent therefore had been lost by evaporation at 100° Fahr.

After some other attempts, I was obliged to conclude that the only way to obtain the dry soluble binacetate in something like atomic proportions, was the unsatisfactory one of evaporating in the air a solution of binacetate, mixed with such a proportion of acetic acid or of teracetate as is found by trial to produce it.

On the question, as to which of the soluble acetates of alumina can be considered as a definite compound, it has already been stated of the teracetate, that when evaporated rapidly enough, and at a heat just low enough to prevent the formation of the insoluble salt, it leaves a product whose composition is nearly that of a binacetate. It may be added, that the solution of teracetate gives off acetic acid as freely in the cold, as if a third part of its acid were free. On making an experiment with two solutions of acetate of lead—one of which was decomposed by sulphuric acid, and the other (which was three times as strong) by tersulphate of alumina—it was found that the aluminous solution gave a smell of acetic acid considerably stronger than that in which the acid was known to be free. It may be doubted, then, whether there exists a combination of acetic acid with alumina corresponding to the tersulphate of alumina. The solution of binacetate has no smell of acetic acid at ordinary temperatures.

BIHYDRATE OF ALUMINA SOLUBLE IN WATER.

$$Al_2O_3 + 2\,HO.$$

Hydrate from the Soluble Binacetate.—By the continued action of heat on a weak solution of binacetate of alumina, a permanent separation of the constituents of the salt takes place, although no acid escapes, and no alumina is precipitated. The properties of the alumina are at the same time materially changed.

A solution of binacetate of alumina, diluted so as to contain not more than 1 part of alumina in 200 of water, was placed in a close vessel which was immersed to the neck in boiling water, and kept in that state day and night for ten days. It had then nearly lost the astringent taste of alum, and acquired the taste of acetic acid. Being afterwards boiled in an open capsule, acetic acid was freely given off, and when the boiling had continued about five hours (the loss of water being continually restored,) the liquid was found to have retained not more than $\frac{1}{11}$ of its original quantity of acetic acid, or about 1 equiv. to $5\frac{1}{2}$ of alumina.

The solution of hydrate of alumina thus obtained has nearly the same transparency as before the loss of its acid, and is slightly oily. It is nearly tasteless. By longer boiling it may be deprived of considerably more of its acid, but there is a danger of coagulation.

A solution containing $\frac{1}{4}$ per cent of alumina is converted into a solid transparent jelly, when mixed with half its bulk of water acidulated with $\frac{1}{2500}$ of sulphuric acid. The jelly has therefore only $\frac{1}{600}$ of its weight of alumina, and $\frac{1}{7500}$ of sulphuric acid.

By pressure in a bag the liquid part of this jelly was readily separated, and the solid was reduced to $\frac{1}{60}$ or $\frac{1}{70}$ of its original volume. Pure water did not dissolve this residue, neither did an excess of sulphuric acid, even at a boiling heat. On examination it was found that the solid portion had imbibed almost the whole of the sulphuric acid. It existed there in the proportion of about 1 equiv. of acid to 15 of alumina.

The coagulating power of the various agents may be ascertained with tolerable accuracy by employing an aluminous solution so dilute as to contain not more than 1 part of alumina in 800 of water, and shaking it in a phial with about half its volume of a coagulating solution. In this manner it was found that 1 atom of citric acid (tribasic) coagulates as powerfully as 3 atoms of sulphuric acid, and tartaric acid (bibasic) as much as 2. 2 atoms of oxalic acid are required to produce the same effect as 1 of sulphuric acid. Of

muriatic and nitric acids, not less than 300 equivs. must be employed to produce an effect equal to that of 1 equiv. of sulphuric acid—the volume of the acid being always $\frac{1}{2}$ that of the aluminous solution. No acid has the power of redissolving the coagulum.*

Of the other acids which have been tried, the chromic, molybdic, racemic, suberic, salicylic, benzoic, gallic, lactic, cinnamic, butyric, valerianic, carbazotic, camphoric, uric, meconic, comenic and hemipinic acids all coagulate the solution; but their exact power has not been ascertained.

The acetic, formic, boracic, arsenious, and cyanuric acids do not coagulate, at least when moderately concentrated; and, of the opium acids, for a supply of which I am indebted to Professor Anderson, the pyromeconic and opianic acids also do not coagulate.

The alkalies have a strong coagulating power. About 2 equivs. of potash produce an effect equal to 1 of sulphuric acid, and the same is the case with soda, ammonia, and lime. The coagulation takes place before the acetic acid which remains in the aluminous solution is fully saturated; for when the alkali, in a very dilute state, is added with caution, the coagulum which it produces has still an acid reaction. This coagulum, like that from sulphuric acid, is insoluble in any acid, whether cold or hot, as well as in pure water. It dissolves, however, in a boiling solution of potash or soda, and when the alkaline solution is afterwards saturated by an acid, the ordinary terhydrate of alumina is thrown down.

Large quantities, however, of the acetic salts (ready formed) may be added before they coagulate the aluminous solution.† When the solid part of the coagulum produced by a strong solution of acetate of soda was afterwards freed from that salt by pressure, it redissolved in pure water, and the solution was again coagulated by a fresh addition of the salt. An experiment with acetate of lime gave the same result.

The nitrates and chlorides coagulate also with great difficulty.

Solutions of sulphate of soda, magnesia, and lime coagulate as readily as a liquid containing the same quantity of sulphuric acid in the free state. On examining one of these mixtures, the sulphuric

* Since these experiments were concluded, it has been found that by employing a wider and shallower porcelain vessel, it is possible to boil off, in an hour and a half, a much larger proportion of acetic acid than that which is mentioned in the text as being done in five hours; and to obtain a product equally fluid.

† Hence, in preparing the binacetate of alumina, which is to be used in obtaining the bihydrate, it is better to employ an excess of acetate of baryta, than to leave in the solution the slightest trace of sulphuric acid.

acid was found in the solid part of the coagulum, as before, and the alkali in the fluid part, united with the acetic acid which had remained in the aluminous solution after boiling.

The digested solution of alumina which has not been deprived of its acetic acid by boiling, requires about twice as much sulphuric acid to coagulate it as does the boiled solution, and thirty or forty times as much alkali. The coagulation is complete before the acetic acid is entirely saturated.

One of the most characteristic properties of the digested and altered acetate of alumina is its loss of the power of acting as a mordant. The ordinary acetate, as is well known, forms a yellow opaque precipitate with decoction of quercitron. That which has been thoroughly digested is merely coagulated by that decoction—the colour of which is but little altered, and the coagulum is translucent. The same effect is produced with decoctions of logwood, brazil-wood, &c.

Analysis of the Soluble Hydrate of Alumina.—A quantity of the digested and boiled solution of hydrate of alumina, which had been found to contain acetic acid in the proportion of about 1 equiv. to $5\frac{1}{2}$ of alumina was evaporated to dryness at 100° Fahr. From the escape, by that means, of its free acetic acid, the proportion of acid was reduced to 2·76 per cent of the dry residue, or about 1 equiv. of acid to 22 of alumina. Not more, therefore, than $\frac{1}{44}$ of the original binacetate had resisted decomposition in the process of digestion and subsequent boiling, and at least 97·8 per cent of its alumina had been changed into the peculiar hydrate. To deprive it, as much as possible, of the remaining acid, and also of hygrometric water, it was exposed for some time to the heat of boiling water. After losing 16·00 per cent of acid and water, it recovered 14·18 per cent when again exposed during twelve hours to the air.

The product, on being moistened with sulphuric acid, as before described, and heated to whiteness, lost in one experiment 24·9, and in another 24·88 per cent. It consisted therefore of

Alumina	75·11
Water, and a trace of acetic acid . .	24·89
	100·00

and approached to the composition of a bihydrate which requires—

Alumina	74·06
Water	25·94
	100·00

Hydrate from the Insoluble Binacetate.—It has been already mentioned that when the precipitated binacetate is kept for an hour or two in 200 parts of boiling water, it is changed into the soluble binacetate. The substance so produced may be converted, like the original solution, into the peculiar bihydrate. Thirty to thirty-six hours digestion is sufficient to complete the change, for after that time the solution has no longer any taste of alum, and the power of coagulating with acids does not increase. A portion of it was boiled in an open vessel eleven hours, being retained at the strength of ½ per cent of alumina by successive additions of water. The solution remained quite clear, and became very slightly oily. It then contained only about 1 equiv. of acetic acid to 19 of alumina. This preparation may be considered as free from all other foreign matter, with the exception of a trace of iron, which still adheres to it. As compared with the solution prepared at once from the soluble binacetate, smaller quantities of the reagents are sufficient to coagulate it, and the coagulum produced has not more than half the density. 0·03 gr. of sulphuric acid, or 0·06 gr. of sulphate of soda is sufficient to coagulate 1·5 grs. of alumina in 600 grs. water, being in the proportion of about 1 equiv. of sulphuric acid to 35 of alumina. An equal quantity of the solution was completely coagulated by 0·034 gr. of potash and by 0·020 gr. of ammonia. In both of these experiments the acetic acid was not fully saturated. The alkalies then are equivalent in coagulating power to sulphuric acid when a very small quantity only of acetic acid is present in the solution.

6·93 grs. of this hydrate, which had been dried at a steam heat, were moistened with sulphuric acid, which was then gradually expelled by a spirit-lamp, and the residue, when kept forty minutes at a white heat, left 5·20 grs. of alumina, showing that the hydrate was composed of—

Alumina	75·03
Water	24·97
	100·00

and contained, therefore, 2 equivs. of water, like the hydrate obtained directly from the soluble binacetate.

ACETATE OF SESQUIOXIDE OF IRON.

The analogy between the salts of alumina and those of the red oxide of iron, induced me to inquire whether there might not exist allotropic acetates of iron, corresponding with those of alumina.

A solution of sulphate of iron, to which was added ½ an equiv. of sulphuric acid, was acted upon by strong nitric acid, and the tersulphate so obtained was converted into the teracetate by decomposition with neutral acetate of lead. A binacetate was also produced by decomposing with a mixture of acetate and carbonate of lead. Both solutions had the same intense red colour which is peculiar to the peracetate of iron.

The teracetate of iron, whether concentrated or weak, is little liable to decomposition in the cold. Boiling causes the deposition of a hydrated peroxide, but the decomposition is only partial, and the hydrate difficult to collect.

The binacetate soon begins to let fall an oxide in the cold; and at the heat of boiling water a complete separation takes place. A rich, deep-coloured hydrate goes readily down, and the whole of the acetic acid remains in the liquid, which is perfectly colourless. No allotropic acetates of iron, corresponding to those of alumina, appear therefore to exist.

BIBASIC SULPHATE OF ALUMINA.

$$2\,Al_2O_3,\,SO_3 + 10\,HO.$$

It is well known that when teracetate of alumina is boiled along with sulphate of potash, a gelatinous precipitate is formed, which redissolves when the solution becomes cold. M. Kœchlin-Schouch* found it to be a subsulphate of alumina.

When alum, dissolved in six times its weight of water, was treated with 3 equivs. of acetate of lead—enough to decompose its tersulphate of alumina, but not the sulphate of potash, a large proportion (74 per cent) of the sulphate of potash was found to be carried down by the sulphate of lead formed in the process. To a solution so prepared, the loss was restored by an addition of sulphate of potash, and a mixture formed of—

$$KO,\,SO_3 \text{ together with } Al_2O_3,\,3\,\bar{A}.$$

This solution, diluted so as to contain about 0·3 per cent of alumina, (from 5 oz. of alum per gallon,) was exposed to heat. At about 90° Fahr., the gelatinous precipitate began to form; and after two hours' boiling, when scarcely a trace of alumina remained in solution, it was thrown upon a filter of calico, which was kept hot within a steam-pan until the filtrate passed through. The collected precipitate was pressed between numerous folds of bleached calico, and brought

* Sur le Mordant Rouge, &c. Bulletin de la Société Industrielle de Mulhausen, I, 299.

gradually to the state of a stiff clay occupying not more than $\frac{1}{40}$ of the volume of the original solution. It was then divided into portions which could conveniently be shaken and thoroughly mixed in bottles with quantities of water equal in all to the original solution. The mixture was filtered as before, at nearly a boiling heat, and pressed between folds of calico; and another repetition having been made of the same process, the precipitate was deprived of every admixture of soluble matter.

A portion being dissolved in nitric acid and filtered, gave an abundant precipitate with nitrate of baryta. Exposed to a white heat, and the residue pulverized and boiled in water, the filtered liquor gave no longer a precipitate with nitrate of baryta, and no indication, or a very doubtful one, of alkali to litmus-paper; proving that the sulphuric acid indicated by the first test had been combined, not with potash, but with alumina. Mixed with sulphuric acid, the substance gave no smell of acetic acid, and when burned with oxide of copper it yielded no more carbonic acid than could readily be accounted for by the few fibres of cotton-wool that were to be distinguished in the liquid. The substance dried into a hard, whitish, semi-transparent matter, easily pulverized.

For analysis, 33·93 grs. dried at 100° Fahr. were dissolved in muriatic acid, and the solution was exactly decomposed at a boiling heat by 15·25 grs. of chloride of barium.* This indicates 5·867 grs., or 17·29 per cent of sulphuric acid. 19·715 grs. mixed with 16 grs. of sulphuric acid in a platinum crucible were first heated with a spirit-lamp, and then exposed to a white heat. It left 8·51 grs. = 43·16 per cent of alumina. Another experiment gave 42·94 per cent. The mean is 43·05. The composition of the substance is therefore—

Sulphuric acid . . .	17·29	SO_3 . . .	17·18
Alumina	43·05	$2\,Al_2O_3$ . .	44·16
Water	39·66	10 HO . .	38·66
	100·00		100·00

* The heat in this case greatly facilitates the arrival at the nearest point of decomposition, particularly by enabling the filter to furnish, immediately, clear portions, from time to time, for testing. Where nitrate of baryta is employed for decomposing a sulphate, it was observed by Mitscherlich that a quantity of the nitrate was taken down unaltered by the sulphate of baryta. This source of error, which amounts to no less than 5 per cent of the quantity of sulphuric acid when the experiment is performed in the cold, is entirely obviated at a boiling heat. Boiling, however, does not render the decomposition of a sulphuric salt by a salt of baryta complete without a considerable excess of the barytic salt, and *vice versâ*. The point sought for in the present instance is that at which *an equal precipitate is formed on adding an excess of either salt.*

When the solution from alum and sugar of lead was heated before the restoration of its sulphate of potash, a very slight precipitate was formed. The addition of that salt completed the precipitation, but the substance thrown down was more transparent, and dried into a brownish, horny-looking matter. Its analysis, however, gave nearly the same results.

Sulphuric acid . . .	17·23
Alumina	43·51
Water	39·26
	100·00

But when the solution was boiled for two hours before the addition of the sulphate of potash, a quantity of alumina seems to have gone down with the sub-sulphate, for its analysis gave in 100 parts

Sulphuric acid . . .	13·73
Alumina	50·71

It had an appearance similar to the preceding product. In the moist state the sub-sulphate is soluble in cold acetic acid, as well as in the mineral acids. It dissolves in 3 atoms of sulphuric acid to form 2 of the bisulphate, which, on the addition of water is resolved into the tersulphate of alumina, and the insoluble monosulphate.

$$2\,Al_2O_3,\,SO_3 + 3\,SO_3 = 2\,(Al_2O_3,\,2\,SO_3).$$
$$= Al_2O_3,\,SO_3 + Al_2O_3,\,3\,SO_3.$$

The same mixture of teracetate of alumina and sulphate of potash, which in a diluted state produces subsulphate of alumina on the application of heat, gives a precipitate of binacetate of alumina when heat is applied to it in a concentrated state. A quantity of sulphate of potash, however, adheres to the insoluble binacetate even after abundant washing.

PRECIPITATE FROM ACETATE OF ALUMINA WITH CHLORIDE OF SODIUM.

A solution of teracetate of alumina was produced from 1 pound of acetate of lead in 10 pounds of water, decomposed by tersulphate of alumina. After purification, common salt was added to it in the proportion of 1 equiv. to 1 of tersulphate of alumina. The solution, when heated in the water-bath, became of an opaque white from the deposition of a powder so very fine that the mixture passed through the filter almost without change. Neither heat, nor any other application could alter this character. It was left at rest, and after some

weeks, the liquid having become nearly clear, was poured off, and the precipitate, which had contracted into $\frac{1}{64}$ of the bulk of the liquid was mixed again with fresh water 11 times its volume. After several weeks more, the precipitate fell again to the bottom of the vessel, when it was mixed with a third portion of fresh water, which again, after four weeks, was decanted, and the precipitate dried in a capsule at 100° Fahr.

On analysis it yielded the following results—I do not give the details of the experiments, not having made out a formula which can be stated in atomic proportions:—

Alumina	44·66
Acetic acid . . .	21·96
Hydrochloric acid . .	5·51
Water	25·90
	98·03
Chloride of sodium . .	1·97
	100·00

Nitrate of potash forms a precipitate when heated with acetate of alumina, similar in appearance to that from common salt, but it was not particularly examined.

CONCLUSIONS.

1. The aluminous solution obtained by decomposing pure ter-sulphate of alumina with the neutral acetate of lead consists, I believe, of a mixture of binacetate of alumina, with an equivalent of free acetic acid. No true teracetate of alumina appears to exist.

2. When means are taken to evaporate the preceding aluminous solution at a low temperature with sufficient rapidity, a dry substance is obtained, which may be redissolved easily and entirely by water. This is the binacetate of alumina, $(Al_2O_3, 2C_4H_3O_3 + 4HO)$, in which the alumina retains all its usual properties.

3. When the first aluminous solution, containing not less than 4 or 5 per cent of alumina, is left for some days in the cold, a salt is deposited in the form of a white crust, which is an allotropic binacetate of alumina, insoluble in water. Heat effects the same change in the aluminous solution more rapidly, and the new acetate then precipitates as a granular powder. At the boiling temperature, the liquid is thus deprived, in about half an hour, of the whole of its alumina, which goes down with two-thirds of the acetic acid; leaving one-third in the liquid.

4. The red acetates of iron treated in a similar manner do not produce corresponding isomeric binacetates. By boiling the binacetate of the sesquioxide there is a total separation of acid and base.

5. The soluble binacetate of alumina is decomposed by heat, and affords a new and remarkable product. When a dilute solution of that salt is exposed to heat for several days, the whole acetic acid appears to become free, and the alumina to pass into an allotropic condition, in which, although it remains in solution, it ceases to be capable of acting as a mordant, or entering into any other definite combination. Indeed alumina in this altered state appears to be truly soluble in pure water. The allotropic alumina retains 2 equivs. of water, when dried at the heat of boiling water. Its solution is coagulated by the mineral, and most of the vegetable acids; by the alkalies; by a great number of neutral salts; and by decoctions of dye-woods.

This alumina is insoluble in the stronger acids, but soluble in acetic acid as well as in pure water, unless it has been previously coagulated by the means above mentioned, when it remains insoluble. It yields, however, to the continued action of boiling potash, which changes it into the ordinary terhydrate. Its coagulum with dye-woods has the colour of the infusion, but is translucent and entirely different from the dense opaque lakes which ordinary alumina forms with the same colouring matters.

6. The insoluble binacetate of alumina, when digested in a large quantity of water, is gradually changed into the soluble binacetate; of which a part, however, becomes decomposed during the process into acetic acid and the allotropic bihydrate of alumina.

7. The precipitate which is formed on the application of heat to a mixed solution of acetate of alumina and sulphate of potash, and which is soluble in cold acetic acid, is a bibasic sulphate of alumina.

NOTICES

OF

PAPERS CONTAINED IN OTHER JOURNALS.

By HENRY WATTS, B.A., F.C.S.

Researches on the Quantities of Heat disengaged in Chemical and Molecular Actions.*

By P. A. Favre and J. T. Silbermann.

Part I.—Heat disengaged in rapid combustion.

The apparatus in which the combustions were performed, consisted of a vessel of gilt brass plate, immersed in a water-calorimeter of silvered copper-plate. The oxygen gas previously dried, was made to flow into the combustion-chamber; and the gases produced by the combustion, were forced, previous to their exit from the calorimeter, to traverse a spiral tube of thin copper, so that they might be completely cooled down to the temperature of the water in the calorimeter. This water, whose volume was about 2 litres, was kept in constant motion by a peculiar apparatus, and thereby maintained at a constant temperature throughout its whole mass. The calorimeter was surrounded with two similar vessels, the outer interval thus formed being filled with water, and the inner, or that which was next to the calorimeter, with swan-down, whereby the loss of heat by external conduction was reduced to a very small and perfectly constant

* Ann. Ch. Phys. [3], XXXIV, 357; XXXVI, 5; XXXVII, 405; Compt. Rend. XVIII, 695; XX, 1565 and 1734; XXI, 944; XXII, 483, 823, 1140; XXIII, 199, 411; XXIV, 1081; XXVI, 595; XXVII, 56, 111, 158, 362; XXVIII, 627; XXIX, 449; Jahresber. 1847—8, 52, 55; 1849, 23, 27; 1852, 17.

quantity, viz., 0·002° for a difference of 1° C. between the water in the calorimeter and the external water.

Solid bodies were set on fire by the introduction of small pieces of burning charcoal; liquids were burned in small lamps with asbestus-wicks; gases were introduced into the combustion-chamber in jets, previously set on fire; charcoal was disposed in a layer on a sieve-formed bottom, through the openings of which the oxygen had free access to it. In experimenting with many difficultly combustible substances, such as sugar-charcoal, it was necessary, in order to ensure continuous combustion, to add a quantity of wood-charcoal; the heat of combustion of this substance was then deducted from the total result.

The rise of temperature of the water in the calorimeter was read off, at stated intervals measured by a Breguet's chronometer, by means of a cathetometer, which gave the measurements to $\frac{1}{20}$ of a millimeter, whilst a degree of the thermometer attached to the calorimeter, occupied a length of 8 millimeters.

The weight of the substance burnt was determined, when possible, not by direct weighing of the body before and after combustion, but from the weight of the products of combustion.

The following are the results of the investigation. The units are the gramme, and the quantity of heat required to raise the temperature of 1 grm. of water from 0° to 1° C.

1 gm. of Hydrogen in combining with Oxygen evolves 34462 heat-units.
1 „ „ „ Chlorine „ 23783 „

Carbon.—As the combustion of carbon in the calorimeter never produced pure carbonic acid and carbonic oxide, it became necessary, first to ascertain the heat of combustion of carbonic oxide, in order to apply the proper corrections to the observations made upon carbon itself. The carbonic oxide was burnt, according to Dulong's process, mixed with hydrogen; the gaseous mixture produced by the combustion was analysed, and the heat of combustion of the hydrogen deducted. The results were as follows:

1 grm. carbonic oxide in combining with oxygen evolves 2403 heat-units.
1 „ wood-charcoal „ „ „ 8080 „
1 „ sugar-charcoal „ „ „ 8040 „

It is interesting to compare the heat of combustion of different kinds of carbon with their specific heats, as determined by Regnault:

	Heat of Combustion for 1 grm.	Specific heat.
Wood-charcoal	8080·0	0·24150
Coke from gas-retorts . . .	8047·3	0·20360
Native graphite	7796·6	0·20187
Graphite from blast-furnaces .	7762·3	0·19702
Diamond	7770·0	0·14687

From this it appears that the heat of combustion of carbon increases with its specific heat.

Hydrocarbons.—1 grm. marsh-gas evolved 13063 heat-units; compounds of the formula $n\,(C_2\,H_2)$ gave the following values:

Olefiant gas . . .	$C_4\,H_4$	11858 heat-units.
Amylene	$C_{10}\,H_{10}$	11491 ,,
Paramylene . . .	$C_{20}\,H_{20}$	11303 ,,
The compound . .	$C_{22}\,H_{22}$	11262 ,,
Cetene	$C_{32}\,H_{32}$	11078 ,,
Metamylene . . .	$C_{40}\,H_{40}$	10928 ,,

Hence it appears that the heat of combustion diminishes, the oftener the group of atoms $C_2\,H_2$ enters into the compound. Favre and Silbermann have constructed a curve which exhibits this decrease to the eye; and, from a comparison of amylene with metamylene, they infer that each addition of $C_2\,H_2$ causes a decrease of 37·5 heat-units. Hence the following table:

Compound.	Heat of Comb.	Compound.	Heat of Comb.
20 $(C_2\,H_2)$	10928·5	10 $(C_2\,H_2)$	11303·5
19 ,,	10966·0	9 ,,	11340·0
18 ,,	11003·5	8 ,,	11378·5
17 ,,	11041.0	7 ,,	11415·0
16 ,,	11078·5	6 ,,	11453·5
15 ,,	11116·0	5 ,,	11491·0
14 ,,	11153·5	4 ,,	11528·5
13 ,,	11191·0	3 ,,	11565·0
12 ,,	11228·5	2 ,,	11603·5
11 ,,	11266·0	1 ,,	11640·0

The difference between the calculated heat of combustion of olefiant gas and that determined by experiment, is explained by the fact that the calculation is based upon data afforded by the combustion of liquids, and consequently, the quantity of heat required to retain the compound in the gaseous state, ought to be added.

Ethers and Alcohols.—Common ether evolved 9027·6 heat-units; amylic ether 10188.

Methyl-alcohol evolved 5307·1; common alcohol 7183·6; amylic alcohol 8958·6; and cetylic alcohol 10629·2. From these data

the following table is constructed for the various bodies of the series $n\,(C_2\,H_2)+2\,HO$.

Compound.	Heat of Comb.	Compound.	Heat of Comb.
20 $(C_2\,H_2)+2$ HO	11000·0	10 $(C_2\,H_2)+2$ HO	10000·0
19 „	10910·0	9 „	9850·0
18 „	10816·0	8 „	9680·0
17 „	10723·0	7 „	9480·0
16 „	10629·0	6 „	9240·0
15 „	10535·0	5 „	8958·6
14 „	10440·0	4 „	8560·0
13 „	10345·0	3 „	8020·0
12 „	10245·0	2 „	7184·0
11 „	10130·0	1 „	5301·5

1 grm. of acetone evolved in combustion 7303 heat-units.

Fatty acids.—Formic acid evolved 2091, acetic acid, 3505·2, butyric acid 5647·0, valerianic acid 6439·0, cetylic acid 9316·5, stearic acid 9716·5, and the curve which represents the increase of these numbers agrees with the following table:

Compound.	Heat of Comb.	Compound.	Heat of Comb.
20 $(C_2\,H_2)+O_4$	9940	10 $(C_2\,H_2)+O_4$	8320
19 „	9820	9 „	8060
18 „	9700	8 „	7780
17 „	9560	7 „	7430
16 „	9420	6 „	7000
15 „	9270	5 „	6439
14 „	9130	4 „	5623
13 „	8950	3 „	4670
12 „	8750	2 „	3505
11 „	8530	1 „	1915

Compound Ethers.—These compounds, which are isomeric with the fatty acids, yielded the following results:

Formiate of methyl . .	$2\,(C_2\,H_2)+O_4$	4197·4 heat-units.
Acetate of methyl . .	$3\,(C_2\,H_2)+O_4$	5342·0 „
Formiate of ethyl . .	$3\,(C_2\,H_2)+O_4$	5278·8 „
Acetate of ethyl . . .	$4\,(C_2\,H_2)+O_4$	6292·7 „
Butyrate of methyl . .	$5\,(C_2\,H_2)+O_4$	6791·5 „
Butyrate of ethyl . . .	$6\,(C_2\,H_2)+O_4$	7090·9 „
Valerate of methyl . .	$6\,(C_2\,H_2)+O_4$	7375·6 „
Valerate of ethyl . . .	$7\,(C_2\,H_2)+O_4$	7834·0 „
Acetate of amyl . . .	$7\,(C_2\,H_2)+O_4$	7971·2 „
Valerate of amyl . . .	$10\,(C_2\,H_2)+O_4$	8543·6 „
Ethylate of cetene . .	$32\,(C_2\,H_2)+O_4$	10342·2 „

These numbers show that bodies isomeric in composition, do not

evolve equal quantities of heat in combustion. This conclusion is confirmed by the following numbers:

Compound.		Heat of Combustion.
Terebene	$C_{20}H_{16}$	10662
Oil of turpentine .	$C_{20}H_{16}$	10852
Oil of lemons . .	$C_{20}H_{8}$	10959

Hydrate of phenyl evolved 7842·3 heat-units.

Sulphur.—Especial care was devoted to the determination of the heat given out by the combustion of sulphur in its various molecular states. The results were as follows:

	Heat-units.
Sulphur fused seven years before the experiment . . .	2216·8
„ heated to the softening point, three months before the experiment	2213·8
„ crystallized from sulphide of carbon	2225·8
„ crystallized from persulphide of hydrogen . . .	2229·5
Native sulphur from Sicily in fine crystals	2220·9
Mean	2220·5
Melted sulphur, burnt several hours after crystallization .	2260·3
Native opaque sulphur	2249·0
ditto	2274·6
ditto mixed with reddish crystals . . .	2337·1

The difference of 40 units between the heat of combustion of sulphur crystallized a long time before the experiment, and that of sulphur crystallized but short time before, is beyond any possible limit of error, and must therefore be due to the different molecular constitution of the two varieties.

The combustion of sulphide of carbon yielded 3400·5 units, whereas, if the heat of combustion of the elements be separately calculated, as it would be if they were in the uncombined state, the result is 3146·3 units. The heat required to bring the elements into the state in which they can combine, must evidently be greater than that which is evolved in the act of combination.

Part II.—Examination of certain phenomena of chemical decomposition and of modifications by dimorphism.

It is generally supposed that when the elements of any compound separate from each other, a quantity of heat is absorbed equal to that which was evolved in their combination; and this supposition is confirmed by experience in a great number of instances. Nevertheless, it is not universally true that chemical decomposition is accompanied by absorption of heat; there are bodies which evolve

heat in decomposing. This is shown, for example, in the combustion of charcoal in nitrous oxide.

1 grm. of charcoal burnt in nitrous oxide, evolved 11158 heat-units, considerably more therefore than when burnt in oxygen. Hence it appears that *in the separation of oxygen from nitrogen, heat is not absorbed, but evolved;* and by comparison of the quantities of heat evolved by the combustion of charcoal in oxygen and in nitrous oxide, it appears that in the separation of 1 grm. of oxygen out of nitrous oxide, 1154 units of heat must be evolved.—The authors likewise endeavoured to estimate the quantity of heat evolved in this separation, by decomposing nitrous oxide into nitrogen and oxygen in the calorimeter by the heat of burning charcoal, and deducting the heat of combustion of the charcoal from the total effect observed. By this method they found that 1 grm. of oxygen in separating out of nitrous oxide, evolves 1090·5 heat-units.

Experiments on the separation of oxygen from peroxide of hydrogen by the action of immersed platinum, made in a mercury-calorimeter of peculiar construction (*vide* p. 240), gavefor the separation of 1 grm. of oxygen, an evolution of 1303 units as a mean result. The numbers obtained in 5 experiments were 1349, 1264, 1313, and 1288; and the authors are of opinion that the highest number 1349, is nearer to the truth than the mean, because the disengagement of oxygen was very difficult to regulate, and was generally too rapid to allow the gas to give off all its heat to the calorimeter. Moreover, this number, 1349, requires an addition of 14° for the heat rendered latent in the aqueous vapour carried off by the gas. Hence the quantity of heat evolved in the separation of 1 grm. of oxygen from peroxide of hydrogen, is 1363 units.

The decomposition of oxide of silver by heat, gave results which did not agree very well with each other. As a mean result it was found, that in the decomposition of 1 grm. of oxide of silver, 21·1 units of heat were absorbed. As one of the elements assumes the gaseous form, the small absorption of heat would seem to show, that in the separation of oxygen from silver, heat is likewise evolved.

Decomposition of Calcspar and Arragonite.—The experiments were made in the water-calorimeter.

In the decomposition of 1 grm. of calcspar by heat, 308·1 units of heat were *absorbed.*

In the transformation of 1 grm. of calcspar into arragonite, 39·1 units were *evolved.*

In the decomposition of 1 grm. of arragonite, 299·3 units were *absorbed.*

The authors likewise examined by polarized light the course of the transformation of arragonite into calcspar, and found that when a crystal of arragonite is heated, the two poles of the lemniscate seen on examining the crystal by polarized light, gradually approach each other, and the closed curves around each pole also approximate

and open out one after the other, so as to form single curves enclosing both poles; but before the union of the two poles was complete, the crystal became opaque.

Part III.—Combinations in the humid way.

Most of the experiments to be detailed in the remaining part of this paper were made in a *mercury-calorimeter*. This instrument may be regarded as a thermometer with a very large reservoir of mercury, and capable of receiving within it the bodies by which the heat is evolved or absorbed. It consists of a glass globe of the capacity of about 1 litre, and having three apertures, one at the top and two at the sides. Into one of the lateral apertures is fixed, in a slanting position, a tube of thin iron, or platinum, closed at the bottom; and into this tube, which is called the *muffle*, is introduced another tube of very thin glass containing the substances which are to be submitted to experiment; it is fused into the metal tube by a cork. At the second lateral aperture, the globe is drawn out into a neck which curves vertically upwards, and into the neck is inserted the bent extremity of a horizontal capillary-tube, the use of which is to measure the changes of volume of mercury in the globe. Through the upper aperture of the globe passes a steel piston moved by a screw, for the purpose of bringing the extremity of the mercurial column in the horizontal tube to any desired point. (For the method of graduation we must refer to the memoir).

Hydration of Sulphuric Acid.

The quantities of heat evolved by mixing 1 grm. of sulphuric acid, SO_3, HO, with various proportions of water are as follows:

Water in equivalents.	Heat-units.	Differences.
With the first $\frac{1}{8}$ equiv. of water . . .	9·4	
„ second $\frac{1}{8}$ „ „ . . .	8·8	0·6
„ first $\frac{1}{4}$ „ „ . . .	18·8	
„ second $\frac{1}{4}$ „ „ . . .	17·2	1·6
„ first $\frac{1}{2}$ „ „ . . .	36·7	
„ second $\frac{1}{2}$ „ „ . . .	28·3	8·4
With 1 equiv. of water	64·7	
„ 2 „ „	94·6	29·9
		17·3
„ 3 „ „	111·9	
		10·3
„ 4 „ „	122·2	
		8·5
„ 5 „ „	130·7	
		5·5
„ 6 „ „	136·2	

Water in equivalents.	Heat-units.	Differences.
With 6 equivs. of water	136·2	5·6
„ 7 „ „	141·8	
		3·3
„ 8 „ „	145·1	
		3·4
„ 9 „ „	148·5	
		0·0
„ 10 „ „	148·4	
		0·0
„ 20 „ „	148·6	

1 grm. of SO_3, 2 HO mixed with water evolves :

With the first	¼ equiv. of water	9·2	1·4
„ second	¼ „ „	7·8	
„ first	½ „ „	17·2	4·9
„ second	½ „ „	12·3	
Therefore with 1 equiv.		29·6	

1 grm. of SO_3, 3 HO mixed with water evolves :

With the first	½ equiv. of water	9·5	1·9
„ second	½ „ „	7·6	
Therefore with 1 equiv.		17·1	

In operating on fractions of equivalents of water, the authors' object was to ascertain whether 1 equiv. of water could unite with 1, 2, 3, 4, &c., equivs. of hydrated sulphuric acid in the same manner as 1 equiv. of water combines with 2 equivs. of anhydrous sulphuric acid ; the results just given justify the anticipation.

Heat disengaged by the solution of gases in water :

1 grm.	hydrochloric acid gas	dissolved in water			evolves	449·6 heat-units.
1 „	hydrobromic	„	„	„	„	235·6 „
1 „	hydriodic	„	„	„	„	147·7 „
1 „	sulphurous	„	„	„	„	120·4 „
1 „	ammoniacal gas		„	„	„	514·3 „

Solution of Salts in Water.

The following table contains the quantities of heat absorbed (or evolved) in the solution of 1 grm. of certain salts in excess of water. (The numbers marked + denote heat evolved).

Some of the numbers relate to the solubility of salts which in reality are insoluble or but very sparingly soluble in water. This fiction rests upon considerations which will be explained hereafter. When an insoluble compound is formed by the combination of an acid with a base, in presence of water, and the quantity of heat evolved is different from that which is given out in the combination of another acid with the same base, when the compound is a soluble salt, the difference may generally be attributed to the insolubility of the first mentioned product; and it is this difference which may be represented by the fictitious solubility of the salt. The utility of the numbers thus obtained will be seen in the part of the memoir which treats of the interchanges of heat between chemically equivalent masses (pp. 253—258).

Oxides or metals	Sulphates.	Nitrates.	Chlorides.	Bromides.	Iodides.	Phosphates.	Pyro-phosphates.	Oxalates.	Tartrates.	Acetates.	Carbonates.	Sulphides.
Of potash . . .	35·3	70·5	51·9	37·8	29·2	—	—	39·7	17·3	—	—	anhydrous +96·9
Of soda	49·1	45·5	8·9	—	—	52·3	21·9	—	25·2	28·1	52·7	—
Of ammonia . .	11·1	65·9	65·1	—	—	—	—	—	—	—	—	—
Of lime	24·7	27.1	15·5	—	—	—	—	—	—	3·5	—	—
Of baryta	64·4	—	16·9	—	—	—	—	—	—	—	—	—
Of strontia . . .	—	41·2	24·0	—	—	—	—	—	—	—	—	—
Of zinc	14·8	—	anhydrous +92·2	—	—	—	—	—	—	—	—	—
Of iron (protoxide)	12·1	—	anhydrous +58·3	—	—	—	—	—	—	—	—	—
Of lead	—	14·9	—	—	—	—	—	—	—	14·8	—	—
Of silver	—	31·1	—	—	—	—	—	—	—	—	—	—
Of Uranyl ($U_2 O_2$)	10·7	—	—	—	—	—	—	—	—	—	—	—
Of copper . . .	—	—	bichloride anhydrous +73·7	—	—	—	—	—	—	—	—	—
Of water	—	—	—	—	—	—	—	67·0	19·8	—	—	—
Of potash and water	25·6	—	—	—	—	—	—	62·1	—	19·3	51·5	—
Of potash and soda	—	—	—	—	—	—	—	—	40·0	—	—	—
Of potash and alumina	23·1	—	—	—	—	—	—	—	—	—	—	—
Of potash and protoxide of iron . .	24·5	—	—	—	—	—	—	—	—	—	—	—
Of ammonia and alumina . . .	19·0	—	—	—	—	—	—	—	—	—	—	—

Formation of Neutral Salts.

The annexed table exhibits the quantities of heat evolved by the combination of 1 grm. of a base with equivalent quantities of the various acids. The numbers marked with an asterisk are those which represent the mean of experiments made by precipitation; the other numbers relate to the calorific effect of an acid on a base in solution or previously precipitated.

1 Gramme of Oxide of		Acids in Solution.												Acids in the Gaseous State.		
						Phosphoric.										
		Sulphuric.	Nitric.	Hydrochloric.	Hydrobromic.	Hydriodic.	1-hydrated.	2-hydrated.	3-hydrated.	Formic.	Acetic.	Valerianic.	Citric.	Oxalic.	Tartaric.	Carbonic.	Sulphurous.	Hydrosulphuric.
Protoxides.	Potassium	342·2	329·7	333·1	329·9	333·8	344·3	360·2	378·4	—	297·3	—	290·6	301·2	277·5	274·0	409·3	137·8
	Sodium	520·1	493·2	492·7	489·1	480·8	496·9	505·2	—	429·3	438·7	435·5	425·1	443·6	408·1	—	—	211·3
	Ammonium	565·0	526·7	520·6	—	—	—	—	—	—	486·5	—	—	—	—	—	—	—
	Barium	270·5	202·1	201·4	—	—	—	—	—	—	174·5	—	—	—	—	—	—	—
	Strontium	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	Calcium	669·8	605·1	606·5	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	Magnesium	*712·9	—	—	—	—	—	—	—	—	524·1	—	—	—	—	—	—	—
		723·7	642·4	661·1	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	Manganese	*345·1	—	—	—	—	—	—	—	—	613·5	—	—	—	—	—	—	—
		346·2	310·6	320·7	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	Iron (protoxide)	*302·5	—	—	—	—	—	—	—	—	285·2	—	—	—	—	—	—	—
		306·7	268·4	273·1	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	Zinc	*255·2	—	—	—	—	—	—	—	—	238·6	—	—	—	—	—	—	323·4
		253·0	203·2	202·6	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	Cobalt	*309·3	—	—	—	—	—	—	—	—	188·3	—	—	—	—	—	—	252·1
		310·4	261·6	272·9	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	Nickel	*314·7	—	—	—	—	—	—	—	—	244·1	—	—	—	—	—	—	—
		316·5	274·8	273·6	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	Copper (black oxide)	*193·8	—	—	—	—	—	—	—	—	243·3	—	—	—	—	—	—	—
		194·5	159·5	160·4	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	Cadmium	*157·2	—	—	—	—	—	—	—	—	131·6	—	—	—	—	—	—	474·2
		160·3	126·7	128·1	—	—	—	—	—	—	—	—	—	—	—	—	—	—
	Lead	101·9	82·5	101·1	99·9	133·9	—	—	—	—	117·9	—	—	—	—	—	—	—
	Silver	89·1	53·5	197·9	220·4	275·8	—	—	—	—	64·0	—	—	—	—	—	—	121·5
	Aluminum	644·0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	268·4
1½ Oxides.	Iron (sesquioxide)	249·5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

Acid and Double Salts.

The experiments were made with about 3 decigrammes of potash or soda with 1, 2, or 8 equivs. of acid, in a flask containing 18 cub. cents. of water.

1. Potash with oxalic acid.

1 grm. of potash, diluted with water and saturated with oxalic acid, yielded:

With 1 equiv. of acid	. . . . .	301·2
„ 2 „ „	and a large quantity of water	299·0
„ 2 „ „	and a small quantity of water	367·8
„ 4 „ „	water in flask at 16° . . .	609·4
Full of water at 13°	. . . . .	640·0
„ „ 11°	. . . . .	672·0

2. Soda with oxalic acid.

1 grm. of soda, diluted with water and saturated with oxalic acid, yielded:

With 1 equiv. of acid	. . . . .	443·6
„ 2 „ „	and a large quantity of water	650·3
„ 4 „ „	„ „ „	682·7
The flask full of water saturated with acid	. . .	739·0

3. Potash with tartaric acid.

1 grm. of potash, diluted with water and saturated with tartaric acid, yielded:

With 1 equiv. of acid	. . . . .	277·5
„ 2 „ „	and a large quantity of water	476·9
„ 2 „ „	and a small quantity of water	502·4
„ 8 „ „	and a large quantity of water	506·0

4. Soda with tartaric acid.

1 grm. of soda, diluted with water and saturated with tartaric acid, yielded:

With 1 equiv. of acid	. . . . .	408·1
„ 2 „ „	and a small quantity of water	616·9
„ 4 „ „	and a large quantity of water	411·0
„ 4 „ „	and a small quantity of water	624·9
„ 8 „ „	and a large quantity of water	435·2
„ 8 „ „	and a small quantity of water	618·9

These results appear to show that when a base is mixed with excess of acid in such quantity as not to form a liquid saturated with the resulting acid salt, the quantity of heat evolved corresponds simply to the formation of a neutral salt; but if the liquid is sufficiently concentrated to deposit the first crystals of the acid-salt, a calorific effect is produced which indicates the formation of a new compound. From this it appears probable that an acid may exist in presence of a neutral salt containing the same acid, without combining with it, at all events immediately, as if the molecules offered some resistance to the formation of the new compound. A phenomenon of the same kind appears to be presented by pyrophosphoric and metaphosphoric acid, which, as is well known, may dissolve in excess of water, without immediately passing to the state of PO_5, 3 HO.

The combination of potash with sulphuric and acetic acid likewise presents results similar to those above detailed with oxalic and tartaric acid. Thus, for 1 grm. of potash treated with—

	Sulphuric acid.	Acetic acid.
An equivalent weight of . . .	332·1	296·0
Twice the equivalent weight . .	332·9	294·1

Since a neutral salt may remain dissolved in water in presence of an excess of acid without entering into any combination with it appreciable by the calorimeter, it appeared worth while to inquire whether acid salts, of definite constitution in the crystalline state, may not be decomposed by contact with excess of water. The authors experimented with this view on biacetate, bisulphate, and bisulphite of potash; the first of these does not appear to be decomposed; the second appears to be decomposed by a very great excess of water (which it was necessary to use in order to avoid the separation of the sparingly soluble neutral sulphate); but it is doubtful whether it would be decomposed by a large quantity. The bisulphite appears to be decomposed by water.

In the formation of *bicarbonate of potash*, the second equivalent of carbonic acid, on being added to the first, evolves an additional quantity of heat equal to 78·2 units.

Hydrosulphuric acid, in combining with protosulphide of potassium in solution, evolves the same quantity of heat as in uniting with an equivalent quantity of potash to form a protosulphide. Hence the quantity of heat evolved by hydrosulphuric acid in combining with 1 grm. of potash to form the sulphide of hydrogen and potassium is, $137{\cdot}8 \times 2 = 275{\cdot}6$ units.

Double Salts.—No heat is evolved on mixing the solutions of:

1. Protosulphate of iron and sulphate of potash;
2. Sulphate of alumina and sulphate of soda;

3. Sulphate of alumina and sulphate of potash;
4. Sulphate of alumina and sulphate of ammonia;
5. Tartrate of potash and tartrate of soda;

provided that the quantity of water present is sufficient to prevent the solution from arriving at the limit of solubility of the double salt. It appears then that, as in the case of acid salts, no calorific effect is produced, so long as the double salt which should be formed, remains in solution.

Basic Salts.—The only salts of this class on which the authors experimented, were the acetates of lead. On precipitating 3 equivs. of neutral acetate of lead by 2 equivs. of potash added successively, it was found that the first equiv. of lead set at liberty, evolved, on combining with the neutral acetate, 20·1 units of heat; but the second equiv. of oxide of lead, set free by the second equiv. of potash, caused no perceptible evolution of heat. Hence it appears that the third equiv. of lead in the tribasic acetate enters into combination without appreciable development of heat. This result was confirmed by treating 1 equiv. of the tribasic acetate in solution, with 1, 2, and 3 equivs. of sulphuric acid in succession. It was found, taking account of the heat evolved by the combination of the oxide of lead with the sulphuric acid, that

The first equiv. of PbO, in combining with acetic acid, evolves	22·8 units.
The second	65·9 „
The third	2·2 „

numbers which accord very nearly with the results obtained by the former method.

Combination of Acids with Anhydrous Bases.

1. *Lime.*—One gramme of lime, treated with dilute hydrochloric acid, evolves 750·4 heat-units; but 1 grm. of hydrate of lime, in combining with the same acid, evolves 606·5 units; hence a gramme of lime, in combining with water, evolves 750·4 − 606·5 = 143·9 units of heat.

Experiments have already been mentioned (p. 239) relating to the heat absorbed in the decomposition of calcspar, and to the heat evolved in the disintegration of arragonite. In those experiments the decompositions were effected by the direct action of heat. To ascertain the same quantities in the wet way, the authors decomposed calcspar and arragonite with hydrochloric acid.

A quantity of Calcspar, containing 1 grm. of lime evolved, when thus treated	82·7 units.
A quantity of Arragonite, containing 1 grm. of lime	106·3 „

Hence, as 1 grm. of lime, in combining with hydrochloric acid, evolves

750·4 units, it follows that 1 grm. of lime, in combining with carbonic acid, evolves

To form calcspar	. . 750·4 − 82·7	= 667·7	units.
To form arragonite	. . 750·4 106·3	= 644·1	„

consequently

1 grm. of calcspar in forming, evolves	. .	373·5 units.
1 grm. of arragonite	. . . . .	360·6 „

The difference, 12·9, between these numbers, represents the quantity of heat disengaged by 1 grm. of arragonite, in passing to the state of calcspar. The quantities given by the former method, were, 308·1 units absorbed in the decomposition of calcspar, and 39·1 units evolved in the formation of arragonite. The authors consider the results obtained in the wet way as by far the more trustworthy.

2. *Baryta.*—One gramme of baryta, treated with dilute hydrochloric acid, evolved 392·2 units of heat. Now 1 grm. of hydrate of baryta in solution, evolves in combining with the same acid, 201·4 units. Therefore 1 grm. of baryta, in passing to the state of hydrate, evolves 892·2 − 701·4 = 190·8 units.

3. *Strontia.*—For strontia the corresponding numbers are : 525·6 − 278·9 = 246·7 units.

4. *Oxide of Lead.*—One grm. of anhydrous oxide of lead, treated with dilute nitric acid, evolves 85 units of heat ; with acetic acid, 64·1 units ; quantities equal to those evolved by the hydrated oxide, under similar circumstances.

5. *Oxide of Zinc,* obtained by the combustion of zinc in oxygen, evolves with dilute sulphuric acid, 267·8 units ; with dilute hydrochloric acid, 207·1 units.

6. *Oxide of Copper* precipitated from a hot solution by potash, gives with dilute sulphuric acid, 206·6 units ; with dilute nitric acid, 172·1 units.

Heat produced by the Combination of Metals with Oxygen, Chlorine, Iodine, &c.

These determinations were for the most part made by an indirect process, proceeding on the assumption that the heat absorbed in the separation of any two elements, is equal to that which is evolved in their combination. The experiments were made in the mercury-calorimeter.

Chlorine was made to combine with hydrogen in the calorimeter ; the hydrochloric acid produced was absorbed by a large quantity of water, and the product weighed as chloride of silver.

Of the compounds of chlorine with metals, the only one that was formed directly was that with copper. The other metals were either dissolved in dilute hydrochloric acid, or their anhydrous oxides were made to combine with that acid. The second method may, in some

cases, be used as a check on the first; if, however, the metal itself is not attacked by hydrochloric acid, the second method is the only one which can be applied; in both methods the product remains in solution. To obtain the quantity of heat which belongs to the anhydrous product, it is necessary to add the heat which is absorbed by the solution of the compound in water. The heat of combination of bromides and iodides may be obtained in a similar manner; or it may be deduced from that of the corresponding chlorides, by deducting the quantity of heat evolved in the substitution of chlorine for bromine or iodine.

The quantities of heat evolved in the combination of *metals* with *sulphur* may be found in a similar manner, if the quantity evolved in the combination of sulphur with hydrogen has been previously ascertained. The latter was determined from the calorific effect produced by the action of sulphuretted hydrogen gas on sulphurous acid dissolved in water (an action which is represented by the equation: $SO_2 + Aq + 2\,HS = 2\,HO + 3\,S + Aq$). The alkaline sulphides were obtained by the action of hydrosulphuric acid on the dissolved oxides in excess; and the insoluble metallic sulphides by double decomposition between the alkaline sulphides and the salts of the other metals.

The heat evolved by the combination of the different metals with *oxygen* was determined in three ways: 1. By the action of water on the alkali-metals, in which regard must be had to the calorific effects produced by three causes—viz., the combustion of the metals, the combination of the oxides with water, and the decomposition of the water. 2. By dissolving a metal in dilute hydrochloric acid. 3. By precipitating one metal with another. The results are contained in the following tables:

Table I. Formation of oxides:

Anhydrous	Zinc	1292·75	heat-units.
		1289·88	,,
	Copper	683·90	,,
	Iron	1351·00	,,
	Lead	266·11	,,
	Silver	56·60	,,
In solution	Potassium.	1954·81	,,
	Sodium	3196·11	,,

Table II. Formation of chlorides:

In solution	Potassium.	2489·54	,,
	Sodium	4101·15	,,
	Zinc	1740·51	,,
		1740·80	,,
	Copper	1078·11	,,
	Iron	1905·34	,,

Anhydrous	Lead	430·10	„
	Silver	322·12	„

To obtain the quantities of heat evolved in the formation of the anhydrous chlorides of potassium, sodium, &c., the preceding results must be corrected for the quantities of heat evolved or absorbed in the solution of those anhydrous chlorides (see page 242). In that table the results are given for 1 grm. of the chlorides; they must therefore be calculated for 1 grm. of the metal. These corrections being made, we find for the heat evolved in the combination of 1 grm. of the metals with chlorine, so as to form an anhydrous chloride, the following quantities:

Potassium	2587·7
Sodium	4125·9
Zinc	1547·5
Copper	922·7
Iron	1775·5
Lead	430·1
Silver	322·2

Table III. Formation of bromides:

	In solution.	Anhydrous.
Hydrogen	28404·00	9332·0
Potassium . . .	2188·30	2303·9
	2196·86	2312·5
Sodium	3592·00	—
Lead	—	315·40
Silver	—	237·19

Table IV. Formation of Iodides:

	In solution.	Anhydrous.	
Hydrogen	15004·22	3606·00	absorbed
Potassium . . .	1850·50	1973·20	evolved
	1858·50	1981·20	„
Sodium	3006·20	—	
Lead	—	223·15	
Silver	—	172·70	

Table V. Formation of sulphides:

	In solution.	Anhydrous.
Hydrogen	—	2741·00
Potassium	1306·90	1170·80
Sodium	2101·74	—
Zinc	—	644·31
Iron	—	634·02

	In solution.	Anhydrous.
Copper	—	285·40
Lead	—	91·88
Silver	—	51·15

Formation of Ammonia.—By the action of chlorine on a solution of ammonia, it was found that 1 grm. of hydrogen in combining with nitrogen to form ammonia, evolves 10488·1 heat-units when the ammonia is in solution, and 7576·00 when the ammonia remains in the state of gas.

SPECIFIC AND LATENT HEATS.

The authors have determined, by means of their mercury-calorimeter, the specific and latent heats of various bodies. The specific heats relate to a mean between the boiling-point of the substance and the final temperature of the calorimeter, which differed but little from that of the surrounding air. The following table contains the principal results. The numbers relate to 1 grm. of the substance.

	Specific heat.	Latent heat of vapour.
Water	—	535·77 units.
Bicarbide of hydrogen, from amylic alcohol, boiling between 200° and 210° . .	0·49385 (from 20° to 200°)	59·91 „ (at 205°)
Bicarbide of hydrogen, from amylic alcohol, boiling between 240° and 260° . .	0·49680 (from 20° to 240°)	59·71 „ (at 250°)
Methylic alcohol	0·6713	263·86 „
Common alcohol	0·6438	208·92 „
Amylic alcohol	0·5873	131·37 „
Cetylic alcohol	0·5059	58 48 „
Latent heat of liquid		29·31 „
Common ether	0·50342	91·11 „
Acetate of ethyl	0·48344	105·796
Butyrate of methyl	0·49176	87·322
Essence of turpentine	0·46727	68·734
Sulphurous acid	—	94·560

For iodine the following results were obtained:

Latent heat of vapour	23·95	units.
Heat given off by liquid iodine from 180° to 107°	7·90	„
Latent heat of fusion	11·71	„
Heat given off by solid iodine from 107° to 20° (Regnault). . . .	4·71	„
Specific heat of liquid iodine . . .	0·10822	„
„ „ solid „ . . .	0·05412	„ (Regnault).

HEAT EVOLVED IN THE CONDENSATION OF GASES BY POROUS BODIES.

The experiments were made with wood-charcoal, previously washed with hydrochloric acid, and then strongly ignited. The charcoal was introduced into a small flask provided with a stop-cock, exhausted of air, and enclosed in the calorimeter, and the gas was passed over it from a gasometer. The following results were obtained for 1 grm. of the gases condensed by charcoal:

Hydrochloric acid gas evolves	232·5	heat-units.
Sulphurous „ „ „	139·9	„
Carbonic „ „ „	129·6	„

The quantities of the gases absorbed were also determined, and it was found that 1 grm. of charcoal absorbs of:

Hydrochloric acid gas	69·2	cub. cent.
Sulphurous „ „	83·2	„
Carbonic „ „	45·2	„

HEAT EVOLVED OR ABSORBED BY THE SUDDEN COMPRESSION OR EXPANSION OF VARIOUS GASES.

The heat evolved by the sudden compression of gases is intimately related to their specific heat. In fact, the specific heat of a gas under a constant volume is connected with its specific heat under a constant pressure by the quantity of heat set in motion by the sudden compression or expansion of a given fraction of the original volume, $\frac{1}{278}$ for example, which is the expansion or contraction corresponding to 1° of temperature.

Dulong has determined the ratio between the two specific heats of various gases from the velocity of sound in those gases, according to the well-known formula of Laplace:

$$\frac{c}{c'} = \frac{v^2}{\frac{gh}{D}(1 + 00365 \times t)}.$$

From these results, and from the numbers obtained by Delaroche and Bérard for the specific heats of gases under constant pressure, Dulong concludes that: *When equal volumes of different gases, taken at the same temperature and under the same pressure, are suddenly compressed or expanded by the same fraction of their primitive volume, they evolve or absorb the same quantity of heat. The resulting variations of temperature are in the inverse ratio of the specific heats for a constant volume.*

It appears, indeed, from the experiments of Delarive and Marcet, as well as from those of Delaroche and Bérard, that all the simple gases have equal specific heats when they are compared in equal

volumes, and Dulong's experiments show that for these gases the ratio $\frac{c}{c'}$ is exactly the same. It follows, therefore, that all simple gases, when equally compressed, experience the same rise of temperature.

With respect to other gases it appears, according to existing data, that *the rise of temperature produced in compound gases, when compressed to the same amount, is less as their specific heat is greater.* We are thus led to inquire whether these differences of temperature proceed *entirely* from the difference of calorific capacity in the compound gases.

The exact determination of the calorific effect produced by the sudden compression and expansion of gases is therefore an object of considerable interest; but hitherto the method adopted in these determinations have been very imperfect.

The apparatus used by Favre and Silbermann, consists of a copper pump-barrel, the lower part of which is lined with glass, so that apertures may be made in the copper (without allowing any escape of gas) in order to observe the variations of a Breguet's thermometer placed inside. Pressure is exerted by a solid piston, the rod of which is moved by a lever connected with the rod by a Watt's parallelogram. The course of the piston is limited to parts proportional to the capacity of the cylinder, by projections which stop the motion of the lever. The gases are introduced into the cylinder by two tubes, the one furnished with a stop-cock and soldered into the lower part of the cylinder, the other entering just under the piston when it is at the top of its course.

In the following table, the temperatures inscribed in the several columns are perhaps too low, because the mass of the Breguet's thermometer is very great in comparison with that of the gas which heats or cools it.

The authors propose, in future researches, to eliminate this cause of error by using several Breguet's thermometers having all the same surface but very different masses. The differences in their indications may then, perhaps, furnish a correction by which the numbers in the following table may be reduced to the values which they would have if the mass of the thermometer were infinitely small. It may be useful also to prevent the reflection of the heat at the surface of the thermometer by coating it with lamp-black.

In the following table, the sign + corresponds to a compression (C), and the sign − to a dilatation (D), for the same horizontal line of temperature:

TABLE OF THE THERMOMETRIC RESULTS PRODUCED BY SUDDEN CHANGE OF VOLUME IN GASES.

Order of conductibility.	Gases.		Between $\frac{1}{4}$ atmosphere and $\frac{1}{2}$	Between $\frac{1}{2}$ atmosphere and 1	Between 1 atmosphere and 2	Between $\frac{1}{2}$ atmosphere and 2	Between $\frac{1}{4}$ atmosphere and 2	Variation of temperature for $\frac{1}{273}$ between $\frac{1}{4}$ and $\frac{1}{2}$ atmosphere.	Variation of temperature for $\frac{1}{273}$ between $\frac{1}{2}$ and 1 atmosphere.	Variation of temperature for $\frac{1}{273}$ between 1 and 2 atmosphere.	According to Dulong. Specific heat for constant volume.	According to Dulong. Ratio $\frac{c}{c'}$ of the two specific heats.	According to Dulong. Variation of temperature for a change of volume $=\frac{1}{273}$
2	Air . .	C	+5·6	8·8	13·2	22·0	27·6	0·0204	0·0321	0·0482	1	1·421	0·421
		D	—5·0	7·6	12·8	20·4	25·4						
3	Oxygen .	C	+5·6	9·3	13·2	22·5	28·1	0·0204	0·0339	0·0482	1	1·415	0·421
		D	—4·7	7·6	13·2	20·8	25·5						
1	Hydrogen	C	+9·7	13·8	18·5	32·3	42·0	0·0354	0·0504	0·0675	1	0·407	0·421
		D	—5·0	8·5	13·7	22·2	27·2						
6	Carbonic acid .	C	+4·7	7·3	11·3	18·6	23·3	0·0171	0·0267	0·0412	1·249	0·338	0·337
		D	—4·7	7·3	11·3	28·6	23·3						
4	Carbonic oxide .	C	+5·6	8·6	12·6	21·2	26·8	0·0204	0·0314	0·0460	1	1·428	0·423
		D	—5·0	7·3	12·6	19·9	24·8						
5	Nitrous oxide .	C	+4·7	6·6	11·0	17·6	22·3	0·0171	0·0241	0·0401	1·227	1·343	0·343
		D	—4·8	6·6	11·3	17·9	22·7						

The numbers in the fourth column of figures in this table are the sum of those in the second and third. They comprise the changes of volume from $\frac{1}{2}$ to 2 atmospheres. The numbers in the fifth column are the sum of the numbers in the first three columns; they therefore comprise the changes of volume from $\frac{1}{4}$ to 2 atmospheres. The authors have ascertained by experiments of verification, that the effect of several successive compressions may be added together without introducing any error into the final result.

It will be seen, that the heat produced by the compression of air and the cold produced by its expansion, are not apparently equal. The same is true for all the other gases, being most conspicuous in case of hydrogen. The difference is due to the various degrees of conducting power of the different gases for heat.

The conducting power of a gas may be regarded as greater or less in proportion to the difference between the amounts of elevation and depression of temperature due to the contraction and expansion. The conducting power of hydrogen appears to exceed that of all other gases as much as that of metals surpasses that of earthy substances. This property of hydrogen appears to account for the rapid cooling of ignited bodies immersed in it, as observed by Andrews and Grove.

The table likewise shows that the elevations of temperature of the compressed gases are nearly in the ratios given by Dulong for each of the gases. Hydrogen deviates from this law, in consequence of its great conducting power.

But the same agreement does not exist with regard to the *absolute* elevations of temperature for each gas referred to a variation of $\frac{1}{278}$ of the original volume, and compared with the corresponding numbers calculated by Dulong from his experiments on the co-efficient $\frac{c}{c'}$, and the numbers obtained by Delaroche and Bérard for the specific heats of gases under constant pressure. This difference arises from the cause already noticed, viz., the diminution in the rise of temperature caused by the mass of the thermometer.

Part IV.—Calorific equivalents.

In the preceding parts of this Memoir, the quantities of heat evolved in chemical combinations have been referred to the unit of weight of one of the combining bodies. More simple and comparable results are, however, obtained by referring them, as we shall now do, to masses proportional to the chemical equivalents of the bodies concerned.

From the data obtained in the third part of these researches (*vide* Table, p. 243), we may form the following table, in which each number represents the sum of the units of heat evolved by a binary compound formed in equivalent proportions, the weight of the equivalent of hydrogen being supposed to be 1 grm. These numbers may be called "Calorific Equivalents;" they represent the heat evolved by the equivalent weight of the resulting compound:

Metals.	Oxides.	Chlorides.	Bromides.	Iodides.	Sulphides.
Hydrogen . .	34462	23783	9322	3606	2741
Potassium . .	—	100960	90188	77268	45638
Sodium . . .	—	94847	—	—	—
Zinc	42451	50296	—	—	20940
Iron	37828	49651	—	—	17753
Copper . . .	21885	29524	—	—	9133
Lead	27675	44730	32802	23208	9556
Silver	6113	24800	25618	18651	5524

These numbers seem to show that the most stable compounds are those whose formation is attended with the greatest evolution of heat.

In order, however, to discuss the relations which may be deduced from a comparison of the calorific equivalents of different compounds, it is necessary to consider these compounds in the state of solution. For the solid state of compounds does not exhibit comparable conditions We do not know how the heat of combination is effected by the crystalline form which a body assumes, or by its state of

cohesion. Everything, in short, tends to show that the conditions of comparability are realized only when the bodies are in the state of solution.

In fact, whatever bromide or iodide, for example, may exist in solution, the quantity of heat evolved by treating it with chlorine is always the same; similarly, when one metal is substituted for another, whatever may be the soluble compound of which it forms part, as among those contained in the following table.

TABLE OF THE CALORIFIC EQUIVALENTS OF BINARY COMPOUNDS IN THE STATE OF SOLUTION.

Metals.	Oxides.	Chlorides.	Bromides.	Iodides.	Sulphides.	Moduli of metals compared with Potassium.	Modulus of each metal compared with the preceding
Hydrogen . .	—	40191	28484	15004	—	−5726	—
Potassium .	76238	97091	85678	72479	50969	—	+57216
Sodium . . .	73510	94326	82616	69143	48340	−2724	−2724
Zinc	—	56567	—	—	—	−40524	−37759
Iron	—	53350	—	—	—	−43741	−3217
Copper . . .	—	34500	—	—	—	−62591	−18850
Moduli of Metalloïds compared with Oxygen .	—	+20834	+9273	−4063	−25219	—	—
Moduli of Metalloïds compared with Chlorine .	—	—	−11637	−24994	—	—	—

A glance at the preceding table, will show that all the calorific equivalents of the compounds in any one vertical column differ from those of the corresponding compounds in the other columns, by a constant quantity, which may be called the *Modulus of the Metalloïds;* it denotes the quantity to be added or subtracted, in order to pass from the calorific equivalent of an oxide, for example, to the calorific equivalent of the corresponding chloride, bromide, &c.

Also that the calorific equivalents of compounds placed on the same horizontal line, differ from the calorific equivalents of the corresponding quantities on any other horizontal line, by a constant quantity, which may be called the *Modulus* of the calorific equivalents of the *Metals.*

The sign — placed before a certain modulus denotes that the calorific equivalents of compounds containing the element assumed as the term of comparison must be subtracted; the sign + indicates that they must be added.

If the state of solution brings the various binary compounds above mentioned to a comparable state, the question is much simplified;

for, if we would ascertain the difference introduced by each metal united to the same metalloïd, it is sufficient to select the soluble binary compounds. On the other hand, if the same metal is combined with several metalloïds, so as to form soluble compounds, the difference caused by each metalloïd will also be known.

It follows, from the experiments above detailed, that nitric, hydrochloric, hydrobromic and hydriodic acid, in combining with the same base, soluble or insoluble, and forming soluble salts, evolve equal quantities of heat. This law we shall generalize, and say that to attribute theoretically to the formation of an insoluble salt the number which would represent its calorific equivalent, apart from its insolubility, it is sufficient to assign to it the same number that would be given by nitric acid, in the formation of a really soluble nitrate with the base in question. The difference between this theoretical number and the real number arises merely from the insolubility.

The following table contains the calorific equivalents of binary compounds, either actually or hypothetically soluble. The numbers followed by a T, are calculated theoretically, according to the conventions above explained:

Metals.	Oxides.	Chlorides.	Bromides.	Iodides.	Sulphides.
Hydrogen	—	40192	28404	15004	—6247 T
Potassium	76238	97091	85678	72479	50969
Sodium .	73510	94326	82616	69143	48340
Zinc . .	35751 T	56567	44857 T	31384 T	10581 T
Iron . .	32554 T	53350	41640 T	28167 T	7364 T
Copper .	13684 T	34500	22790 T	9317 T	—11486 T
Lead . .	21808 T	42661 T	31243 T	18049 T	—3461 T
Silver . .	—2808 T	18049 T	6636 T	—6563 T	—28073 T

By subtracting the numbers in this table from those in the last but one, we obtain differences which represent theoretically the quantity of heat absorbed by the solution of the compounds in question.

To bring these compounds theoretically to the soluble state, is to ascertain the part of the calorific effect due to the change of state.

HEAT ABSORBED IN THE HYPOTHETICAL SOLUTION OF THE FOLLOWING COMPOUNDS.

Metals.	Oxides.	Chlorides.	Bromides.	Iodides.	Sulphides.
Hydrogen . .	—	—	—	—	8988
Zinc	6700	—	—	—	10359
Iron	5274	—	—	—	10388
Copper . . .	8201	—	—	—	20619
Lead	5867	2069	1554	5159	13017
Silver	8991	16751	18982	25214	33597

If we now examine the relation between the heat evolved and the energy of the chemical affinities, the metalloïds above considered must be placed in the following order, according to the compounds of each metalloïd with the same metal: *Chlorine, Bromine, Oxygen, Iodine, Sulphur.*

And the metals will be arranged in the following order, which will be the same whether we consider the series of the oxides, chlorides, bromides, iodides or sulphides: *Potassium, Sodium, Zinc, Iron, Lead, Copper, Silver.*

This order agrees tolerably well with that which would be deduced from a general view of the chemical reactions of these metals and the stability of the compounds formed.

Saline Compounds.—Let us now endeavour to institute a comparison between the quantities of heat evolved by the equivalent weights of various bases in combining with 1 equiv. of the same acid. The table may be formed from the soluble sulphates.

Bases, with 1 equiv. of oxygen (MO).	Equivalents of the bases (H = 1 grm).	Units of Heat evolved by the equivalent of each base in combining with 40 grms. of real sulphuric acid, or 1 equiv.
Potash	47 grms.	16083
Soda	31 „	15810
Oxide of ammonium . .	26 „	14690
Magnesia	20 „	14440
Oxide of manganese . . .	35 „	12075
„ nickel	38 „	11932
„ cobalt	38 „	11780
„ iron	36 „	10872
„ zinc	41 „	10455
„ cadmium . . .	64 „	10240
„ copper	40 „	7720
Bases (M_2O_3).		
Sesquioxide of aluminum .	$AlO\frac{3}{2}=17$	10948
„ iron (or oxide of *Ferricum ?*) . . .	$FeO\frac{3}{2}=27$	6736

These numbers indicate a sufficiently close connection between the energy of the affinities of the various bases for the same acid, or the degree of stability of the compound formed, and the quantities of heat disengaged in the act of combination, these quantities of heat being referred to weights of the various bodies proportional to their chemical equivalents.

Those bases which form insoluble sulphates are not included in the table. In this case, the phenomena are no longer comparable, and the numbers which they would give would be too high.

The following table relates to *Nitrates* formed in presence of excess of water.

Bases of the formula MO.	Equivalents of the bases (H=1 grm).	Units of Heat evolved by an equivalent of each base in combining with 54 grms. of nitric acid.
Oxide of calcium	28 grms.	16943
„ strontium . . .	58 „	16943
„ barium	76 „	15360
„ potassium . . .	47 „	15510
„ sodium	31 „	15283
„ ammonium . . .	26 „	13676
„ magnesium . . .	20 „	12840
„ manganese . . .	35 „	10850
„ nickel	38 „	10450
„ cobalt	38 „	9056
„ iron	36 „	9648
„ lead	112 „	9240
„ zinc	41 „	8323
„ cadmium . . .	64 „	8116
„ copper	40 „	6400
„ silver	116 „	6206

The bases of this table follow one another in the same order, with regard to the heat evolved, as those of the preceding table, which relates to sulphuric acid.

Magnesia and ammonia are tolerably near each other; the oxides of manganese, nickel and cobalt, evolve quantities of heat which are sensibly equal. Oxide of lead, which saturates acids much more completely than the other oxides of the same class, evolves much more heat than oxide of copper.

Sulphuric and phosphoric acid, in combining with bases, evolve more heat than nitric, hydrochloric, hydrobomic and hydriodic acid. Of the three varieties of phosphoric acid, the monohydrated acid evolves the smallest and the terhydrated the largest quantity of heat.

Among the organic acids, oxalic, formic, acetic, valerianic, and citric acids evolve about equal quantities of heat, but less than the mineral acids just mentioned. Lastly, tartaric, carbonic, and hydrosulphuric acid evolve less heat than any other acids. All these peculiarities will be clearly seen by inspection of the following table, the numbers in which express the quantities of heat evolved in the

combination of various acids with bases in equivalent quantities. The table includes only soluble compounds.

Basic Protoxides.	Acids.															
	Sulphuric.	Nitric.	Hydrochloric.	Hydrobromic.	Hydriodic.	Phosphoric. HO	Phosphoric. 2 HO	Phosphoric. 3 HO	Formic.	Acetic.	rianic.	Citric.	Oxalic.	Tartaric.	Carbonic.	Hydrosulphuric.
Potash .	16083	15510	15656	15510	15698	16168	16920	17766	—	13973	—	13658	14156	13425	12878	6477
Soda . .	15810	15283	15128	15159	15097	15407	15655	—	13308	13600	13500	13178	13752	12651	—	6550
Oxide of ammonium .	14690	13676	13536	—	—	—	—	—	—	12649	—	—	—	—	—	—
Magnesia .	14440	12840	13220	—	—	—	—	—	—	12270	—	—	—	—	—	—
Oxide of manganese	12075	10850	11235	—	—	—	—	—	—	9982	—	—	—	—	—	—
Oxide of nickel .	11932	10450	10412	—	—	—	—	—	—	9245	—	—	—	—	—	—
Oxide of cobalt .	11780	9956	10374	—	—	—	—	—	—	9272	—	—	—	—	—	—
Oxide of iron . .	10872	9648	9828	—	—	—	—	—	—	8590	—	—	—	—	—	—
Oxide of zinc . .	10455	8323	8307	—	—	—	—	—	—	7720	—	—	—	—	—	—
Oxide of cadmium	10240	8116	8109	—	—	—	—	—	—	7546	—	—	—	—	—	—
Oxide of copper .	7720	6400	6416	—	—	—	—	—	—	5264	—	—	—	—	—	—

Part V.—Chemical action of the solar rays.

Draper has shown that chlorine, which has been *insolated*—that is, exposed to the direct rays of the sun—will afterwards combine with hydrogen in the dark.

Favre and Silbermann were induced by this result to examine further the modifications produced in chlorine by the action of the solar rays. They have found:

1. That the heat evolved by the action of previously insolated chlorine on caustic potash, is greater than that evolved by the action of non-insolated chlorine, the action in both cases taking place in perfect darkness. 1 grm. of chlorine acting on a concentrated solution of caustic potash, evolves the following quantities of heat:

Insolated chlorine. . . .	478·85	units of heat.
Chlorine not *insolated* . . .	439·70	„
Difference . . .	39·15	„

The authors have also examined the effect produced on a mixture of chlorine and hydrogen, by the various parts of the solar spectrum. Fifty small tubes filled with the mixture, and standing over water, were placed close together in a row, and exposed to a Frauenhofer's spectrum, projected horizontally. By this arrangement each tube was exposed to the action of a single colour. It was found that, in the morning, with a white sky, the maximum

effect was produced towards the fixed line H; in the middle of the day towards G; the maximum effect for the whole day was likewise towards that part; in the evening towards F. The relative effects in the different parts of the spectrum are represented by curves, for which we must refer to the Memoir.

QUANTITIES OF HEAT EVOLVED IN CHEMICAL ACTIONS PRODUCED BY THE ELECTRIC CURRENT.

The result of the authors' experiments on this subject, are comprised in the three following propositions;

1. The time required for the decomposition of a given weight of water, is proportional to the intensity of the current.
2. Those parts of a given circuit which offer equal resistance to the current, evolve equal quantities of heat.
3. When a voltameter and a platinum wire offering equal resistance to the current, are placed in the same circuit, the quantities of heat evolved by the two are equal, provided the heat absorbed by the decomposition of the water is taken into account.

Researches on Didymium and its principal compounds.

By C. Marignac.*

This paper is a continuation of the author's researches on the cerium-metals. In a former Memoir,† he has treated of the separation of the oxides of the three allied metals, and determined the atomic weights of cerium and lanthanum, and approximately that of didymium. To obtain pure oxide of cerium, he treats the mixture of the three oxides, first with very dilute and then with stronger nitric acid, which latter extracts the last traces of lanthanum and didymium. The oxides of the latter metals can also be obtained quite free from cerium by evaporating to dryness the solution obtained with dilute nitric acid, igniting the residue, and again treating it with nitric acid diluted with at least two hundred times its weight of water.—The oxides of lanthanum and didymium were separated one from the other, by Mosander's method, viz., by dissolving the mixed sulphates to saturation in water at 5° or 6° C., and heating the solution to about 30°, whereupon sulphate of lanthanum crystallizes out, while the greater part of the sulphate of didymium remains in solution. By repeated application of this treatment, the sulphate of lanthanum may be

* Ann. Ch. Phys. [3] XXXVIII, 148. † Ibid. XXVII, 209.

obtained pure and colourless; and the sulphate of didymium, separated as above from the greater part of the lanthanum-salt, may be further purified by crystallizing, picking out the darkest coloured crystals, recrystallizing these, and repeating this process several times. In the present Memoir, the author adds that the separation of lanthanum and didymium may be considerably facilitated by first dissolving the oxides in a large excess of nitric acid, and precipitating in several successive portions by oxalic acid; the first precipitates thus formed, are of a much deeper rose-colour and much richer in didymium than the latter. The separation thus effected is very imperfect in itself, but it greatly facilitates the subsequent separation of the sulphates, which is much more rapid when one of the oxides is already in great excess with regard to the other.

The atomic weights of the three metals are determined by ascertaining the quantity of chloride of barium required to decompose a given weight of the sulphates. In this manner the author, in his former Memoir, estimated the atomic weight of cerium at 47·26; that of lanthanum at 47·04; and that of didymium at 49·4.—In the present Memoir he returns to the consideration of the atomic weight of didymium, and states that from trials which he has made of the determination of the atomic weights of other oxides by the same method, he finds that it can never be entirely depended upon, because, in most cases, when a sulphate is precipitated by chloride of barium, the precipitated sulphate of baryta, *even when a large excess of chloride of barium is used*, carries down with it a very sensible portion of the soluble sulphate, and retains it in spite of repeated washing. On applying to his former results, a correction on account of this error, he finds the atomic weight of didymium to be=47·95.

To check this result, another method was used, viz., the precipitation of a solution of the sulphate by oxalate of ammonia. The oxalate of didymium is completely insoluble in a neutral liquid; it washes easily, and does not retain any sulphuric acid. To convert it into protoxide of didymium, it is first roasted, and then strongly ignited by a powerful lamp, or still better, in a furnace, in order to convert the peroxide of didymium into protoxide. This method gives for the atomic weight of the metal, the number 47·85.

Lastly, the atomic weight was determined by the analysis of the chloride. The author found it impossible to obtain a correct result by weighing a portion of the chloride, and determining the chlorine therein, because a solution of the chloride, when evaporated to dryness, gives off a considerable quantity of hydrochloric acid, and leaves a residue partly insoluble in water, the insoluble portion being probably an oxychloride; he therefore, without weighing the chloride, precipitated the chlorine by nitrate of silver, the excess of silver by hydrochloric acid, and then the oxide of didymium by oxalate

of ammonia. A comparison of the weights of the chloride of silver, and oxide of didymium obtained, gave for the atomic weight of the latter, in three experiments, the numbers, 56·26, 55·91, and 55·86, the mean of which is 56·01.

From a comparison of all these results, the author adopts for the oxide the number 56, and consequently for the metal, 48.

The author next proceeds to examine the properties of didymium and of some of its compounds.

Metallic Didymium.—The metal was prepared by heating potassium with an excess of chloride of didymium, in a porcelain tube closed at one end, the chloride having been previously fused with sal-ammoniac. The product was scoriaceous, rather than fused, although it had been subjected to tolerably strong ignition; cold water extracted from it, chloride of potassium and chloride of didymium, and left a greyish pulverulent substance, from which bubbles of hydrogen continually escaped. This residue consisted partly of a grey metallic powder, and partly of a greyish-white crystalline powder, probably oxychloride of didymium. The latter was partially removed by levigation, but the grey powder was not obtained sufficiently pure to take its density. When thrown into an alcohol flame, each metallic particle produced a bright spark like those which accompany the combustion of iron in oxygen. In one of these experiments, there were found in the midst of the pulverulent mass, two small metallic granules, which had probably fused at the first instant of the action of the potassium on the chloride of didymium; they were of an iron-grey colour, with considerable lustre on the fractured surfaces, which however soon tarnished; they flattened a little under the hammer, but soon afterwards broke to pieces. One of these fragments, heated on charcoal before the blow-pipe, did not melt, but after a while was converted into a friable mass of oxide, without having exhibited any particular phenomenon of combustion. These metallic fragments did not appear to decompose water in the cold, but on the following day they were found to be converted into a flocculent mass of oxide, perhaps by the influence of atmospheric oxygen. It appears then that didymium decomposes water at ordinary temperatures when it is in the state of powder, but not after it has been fused. In either case, the addition of an acid instantly gives rise to rapid evolution of hydrogen.

Protoxide.—There appears to be but one oxide of didymium capable of acting as a base, the peroxide giving off oxygen before it dissolves in acids. The protoxide is readily obtained by calcining the nitrate, oxalate, carbonate, or the hydrate precipitated by caustic alkalies. It is brown only when mixed with peroxide; strong ignition renders it perfectly white. Hydrogen has no action upon it at

a red heat, and does not alter its whiteness. When once brought by strong ignition to the state of pure protoxide, it does not become peroxidized, or turn brown by moderate ignition in contact with the air, not even by fusion with nitre; but if a little nitric acid be added to it, and the calcination repeated, the oxide assumes a dark brown colour, which disappears by a stronger calcination.

Protoxide of didymium is a very strong base, but little inferior in this respect to oxide of lanthanum; even after very strong ignition, it dissolves with the utmost facility in the weakest acids, with considerable rise of temperature, and without giving off any gas. It dissolves also in ammoniacal salts at a boiling heat, expelling the ammonia. It rapidly absorbs carbonic acid from the air. Water, with the aid of heat, gradually converts it into a hydrate; but the conversion is not complete till after the lapse of two or three days.

The hydrated oxide precipitated from a solution of the chloride by potash or ammonia, is gelatinous and resembles alumina, but has a very pale rose colour. It is almost impossible to free it completely from chlorine by washing; but the quantity which remains is too small to constitute a basic salt. The hydrate contracts much by desiccation, and assumes a greyish-rose tint. After being dried, first *in vacuo*, and then in a stove at 100°, it loses by strong calcination 15 per cent of its weight. Hence it contains 1 atom of water:

DiO . .	56	86·15
HO . .	9	13·85
DiO, HO . .	65	100 00

It had probably absorbed a small quantity of carbonic acid during desiccation.

The salts of didymium have generally a pure rose colour, like the sulphate, or slightly violet, like the nitrate in a state of strong solution. Caustic alkalies added to the solutions throw down the gelatinous hydrate; the alkaline carbonates and bicarbonates throw down carbonate of didymium completely insoluble in an excess of these reagents; hydrosulphate of ammonia likewise precipitates the hydrate. Carbonate of baryta precipitates oxide of didymium from its salts, slowly but completely, even without the aid of heat. Oxalate of ammonia also throws it down completely from neutral solutions; even oxalic acid precipitates it almost completely, provided the solution does not contain a great excess of a strong acid. The sulphates of potash, soda and ammonia form, immediately in concentrated solutions, and after some time in dilute solutions, rose-white precipitates of double sulphates, slightly soluble in water, and less soluble in an excess of the reagent, but not perfectly insoluble therein; the sodium-salt is the least soluble of the three. Phosphoric and arsenic acids at a boiling heat form precipitates sparingly soluble in acids.

Before the blow-pipe, oxide of didymium imparts to borax and phosphorus-salt a very pale rose colour, like that produced by a very small quantity of oxide of manganese. It does not colour carbonate of soda.

Peroxide.—When oxide of didymium has not been very strongly ignited, it exhibits a reddish-brown colour more or less deep. It is then in the state of peroxide, dissolves in oxygen-acids with evolution of oxygen, and in hydrochloric acid with evolution of chlorine. It dissolves, however, in these acids, even when extremely dilute, absorbs carbonic acid from the air, and expels ammonia from its salts like the protoxide. It is likewise ultimately converted into hydrate by boiling with water; but the change does not become perceptible for several hours.

This oxide may be obtained by roasting the oxalate or the carbonate; but when thus prepared, it always retains carbonic acid, the carbonate requiring strong ignition to decompose it completely. The peroxide may be more conveniently prepared by calcining the nitrate.

This brown oxide does not appear to be a definite compound, the excess of oxygen in it being small and variable, amounting in different preparations to 0·32, 0·49, 0·53, 0·51 and 0·88 per cent. It is probably a mixture of the protoxide with a peroxide of definite composition. It is so easily attacked by acids, that when it is mixed with carbonate, the latter is the last dissolved.

Sulphide.—When protoxide of didymium is calcined with carbonate of soda and excess of sulphur, and the fused mass digested in water, there remains a greyish-white insoluble residue, which, after desiccation *in vacuo*, suffers no loss of weight by ignition in a current of hydrogen.

It dissolves completely in dilute hydrochloric acid, giving off a small quantity of sulphuretted hydrogen. It is not so quickly attacked as the oxide, and does not appear to be separated by this treatment into 2 parts which dissolve one after the other.

Analysis shows it to be, not a sulphide, but an oxysulphide containing 1 atom of sulphide to 2 atoms of oxide:

		Calculated.	Found.	
3 Di . . .	144	81·82	80·58	—
2 O . . .	16	9·09	—	—
S . . .	16	9·09	9·39	8·50
2 DiO, DiS . .	176	100·00		

The pure sulphide of didymium is obtained by passing the vapour of sulphide of carbon carried forward by a stream of hydrogen, over oxide of didymium heated to redness in a porcelain tube. Prepared in this manner, the sulphide does not form a fused mass, but a powder of a light brownish-green colour. When moistened with water, it

exhales an odour of sulphuretted hydrogen, without however giving off bubbles of the gas when immersed in water; it does not dissolve in water. Acids, even when very dilute, decompose it with evolution of sulphuretted hydrogen. Heated on platinum-foil, it becomes ignited like protoxide of tin, and is converted into oxide mixed with subsulphate.

2·742 parts of protoxide, containing 0·392 of oxygen, produced 3·124 of sulphide. Hence the 0·392 of oxygen was replaced by 0·774 of sulphur. The formula DiS requires 0·784.

Chloride.—The solution of oxide of didymium in hydrochloric acid is of a pure rose colour. When sufficiently concentrated by heat, it deposits on cooling, rose-coloured crystals of considerable size, consisting of the hydrated chloride. These crystals are deliquescent, which renders it difficult to determine their form. They are rhomboïdal prisms of 78°, with an oblique base inclined 92° to the faces of the prism.

This chloride is very soluble in water and alcohol. Its solution cannot be evaporated to dryness without giving off hydrochloric acid; and on digesting the residue in water, part of it dissolves, but there remains a white insoluble residue, which is an oxychloride.

The composition of the chloride is as follows:

		Calculated.	Found.
Di . . .	48·0	40·18	40·25
Cl . . .	35·4	29·68	29·70
4 HO . . .	36·0	30·14	31·71
Di Cl, 4 HO . .	119·4	100·00	

The insoluble oxychloride formed by evaporating the chloride to dryness, does not yield constant results on analysis. After drying *in vacuo*, it does not give off water at 100°, but loses from 10 to 11 per cent of its weight by calcination. Prolonged calcination in contact with the air does not appear to expel the chlorine, the compound not turning brown. It was analyzed by dissolving it in cold dilute nitric acid, and determining successively the chlorine and the oxide of didymium, the water being estimated by loss.

		Calculated.	Found.		
DiCl	83·46	37·52	35·60	31·48	36·62
2 DiO	112·00	50·35	53·36	55·64	52·09
3 HO	27·00	12·13	11·04	12·88	11·29
DiCl, 2 DiO + 3 HO	222·46	100·00			

These results show that the products of different preparations have not exactly the same composition, possibly because they contain portions of oxide in the state of simple mixture. After the oxy-

chloride has been exposed for some time to the air, it dissolves in acids with effervescence, which shows that it has absorbed carbonic acid.

Nitrate.—This salt is extremely soluble in water. Its solution is of a pure rose colour when dilute, but appears violet by reflected light when concentrated. A syrupy solution solidifies on cooling in a crystalline mass, but too deliquescent and too much saturated with mother-liquor to admit of a determination of the crystalline form.

It gives off its water with difficulty, not becoming anhydrous till it undergoes the igneous fusion at a temperature above 300° C. If it be very carefully raised to this temperature, it does not decompose, and is still capable of redissolving completely in water. It then exhibits the composition of an anhydrous neutral nitrate.

		Calculated.	Found.
DiO . . .	56·	50·91	50·48
NO_5 . . .	54·	49·09	—
DiO, NO_5 .	110·	100·00	

The anhydrous nitrate dissolves in alcohol of 96 per cent as readily as in water; the solution does not become turbid even on the addition of a large quantity of ether. The salt does not however dissolve in ether alone.

If it be raised to a higher temperature after fusion, it decomposes, giving off copious fumes of hyponitric acid. Soon afterwards it becomes pasty, swells up, and leaves a white, porous, light mass, which subsequently changes to the brown peroxide.

If the residue be treated with water when the decomposition has but just begun, the water dissolves out a portion of neutral nitrate, and leaves a white residue tinged with rose colour. This residue contains nitric acid without nitrous, as may be readily ascertained by treating it with sulphuric acid. The composition of this sub-salt is as follows:

		Calculated.	Found.	
4 DiO . . .	224	69·35	68·75	71·20
NO_5 . . .	54	16·72	17·69	15·19
5 HO . . .	45	13·93	—	—
4 DiO, NO_5 + 5 Aq.	323	100·00		

This product is very probably a mixture of a subnitrate with the protoxide of didymium, hydrated or anhydrous.

Phosphate.—A concentrated solution of phosphoric acid does not produce an immediate precipitate in a strong solution of nitrate of didymium, but at the end of an hour or two, a white, pulverulent precipitate is formed. The addition of a large quantity of water

causes the precipitate to form immediately. The greater part of the oxide of didymium is ultimately carried down in this precipitate. It is insoluble in water, very sparingly soluble in dilute acids, but dissolves readily in the strong acids when concentrated.

After desiccation *in vacuo*, it gives off by calcination 7·02 per cent, or 2 atoms of water. It is tribasic.

		Calculated.	Found.
PO_5 . . .	71	29·71	—
3 DiO . . .	168	70·29	70·19
3 DiO, PO_5 . .	239	100·00	

Arseniate.—Arsenic acid does not precipitate the solutions of didymic salts at ordinary temperatures, even after a considerable time. But on boiling the liquid, a copious precipitate is formed, and very little oxide of didymium remains in solution. Neutral arseniate of potash instantly precipitates didymic salts at ordinary temperatures.

Arseniate of didymium prepared by either of these processes has the same composition. But when precipitated at a boiling heat, it is pulverulent, and remains so after desiccation; when precipitated in the cold, it is slightly gelatinous, and maintains after drying, a certain degree of transparence and a rose colour. It is but slightly soluble in dilute acids.

After drying *in vacuo*, it does not give off any water at 100°, but only by calcination; the proportion thus evolved cannot be precisely determined. For, after the water has been expelled, the salt gradually decomposes by roasting, and diminishes continually in weight. To obtain an exact determination of the water, it is necessary to calcine the salt with a known weight of oxide of lead. The rest of the analysis is made in the usual way, and leads to the following results:

		Calculated.	Found.				
2 AsO_5 . .	230	43·56					
5 DiO . .	280	53·03	52·94	53·34	54·04	53·98	53·50
2 HO . .	18	3·41	3·86	3·88			
5 DiO, 2 AsO_5 + 2 Aq.	528	100·00					

The composition of this salt being somewhat unusual, the analyses were repeated on samples prepared in various ways, sometimes with neutral, sometimes with strongly acid solutions, but always with the same result.

Carbonate.—The alkaline carbonates and bicarbonates produce in salts of didymium, very bulky, white precipitates, tinged with rose colour, completely insoluble in excess of the re-agents, and never appearing to assume the nacreous and lamellated aspect of

the carbonates of cerium and lanthanum, even after long immersion in the liquid in which they are formed.

The carbonate prepared in the cold with bicarbonate of ammonia and nitrate of didymium, and dried *in vacuo*, gave the following results on analysis:

		Calculated.	Found.
DiO	56	58·33	58·39
CO_2	22	22·92	22·95
2 HO	18	18·75	
DiO, CO_2 + 2 Aq. . .	96	100·00	

At 100°, this salt loses 14·36 per cent of its weight, corresponding to 1½ atom of water. But the analysis of the salt thus dried, proves that it has also lost a small quantity of carbonic acid:

		Calculated.	Found.
DiO . . .	56·0	67·88	68·46
CO_2 . . .	22·0	26·66	25·63
½ HO . .	4·5	5·46	
	82·5	100·00	

From this it would appear, that the neutral anhydrous carbonate cannot be obtained by drying the hydrated salt.

Sulphite.—Oxide of didymium, strongly calcined and suspended in water, is readily dissolved by a stream of sulphurous acid gas. The solution is of a pure rose colour. As soon as it is heated, it becomes very turbid, forming a very light and bulky precipitate, which redissolves as the liquid cools. But if the temperature be raised to the boiling-point, so as to expel the excess of sulphurous acid, the precipitate becomes pulverulent, of a rose-white colour, and no longer dissolves on cooling. The liquid retains mere traces of oxide of didymium, due to the formation of a small quantity of sulphuric acid, for the sulphite appears to be quite insoluble.

Suspended in water and exposed to a stream of chlorine, it dissolves readily, and is converted into sulphate; on evaporating the liquid to dryness, a residue of pure neutral sulphate is obtained. When ignited, it gives off sulphurous acid, and is converted into oxide mixed with a small quantity of subsulphate. After drying *in vacuo*, it retains 2 atoms of water, like the carbonate.

		Calculated.	Found.
DiO . . .	56	52·83	53·36
SO_2 . . .	32	30·19	30·42
2 HO . . .	18	16·98	
DiO, SO_2 + 2 Aq. .	106	100·00	

Sulphate.—Formed by dissolving the oxide or carbonate in dilute sulphuric acid. The solution is rose-coloured, and deposits, by spontaneous evaporation, dark rose-coloured, shining crystals, having the form of an oblique rhomboidal prism. The crystals are often macled parallel to the anterior edge of the prism; they cleave readily and distinctly in a direction parallel to the base. They give off their water at 200°, leaving an anhydrous powder which may be heated to redness without undergoing any further alteration.

		Calculated.	Found.
DiO . . .	56	58·33	58·27
SO_3 . . .	40	41·67	
DiO, SO_3 . .	96	100·00	

The crystals differ altogether in form from those of the sulphate of lanthanum, and contain $\frac{1}{3}$ of an equivalent of water less. Crystallized sulphate of lanthanum contains 3 atoms of water; $LaO, SO_3 + 3$ Aq.; but the formula of the rhombic crystals of sulphate of didymium is $3\,(DiO, SO_3) + 8$ Aq.

		Calculated.	Found.
$3\,(DiO, SO_3)$ . .	288	80	
8 HO	72	20	20·2
	360	100	

The formula $DiO, SO_3 + 3$ Aq. requires 21·95 per cent of water.

A solution of the sulphate, when heated, especially to the boiling-point, deposits a crystalline precipitate containing only 2 atoms of water.

		Calculated.	Found.
DiO, SO_3 . . .	96	84·21	—
2 HO	18	15·79	14·76
$DiO, SO_3 + 2$ Aq. . .	114	100·00	

As the separation of lanthanum and didymium depends upon the difference of solubility of their sulphates, the author endeavoured to determine this point with some degree of exactness for the sulphate of didymium. Somewhat different results are obtained, accordingly as the anhydrous salt or either of the hydrates is dissolved, as may be seen by the following table, although the experiments were not made at exactly the same temperatures. The experiment was always commenced by dissolving the salt of saturation in cold water, then keeping the temperature stationary at higher and higher degrees, and each time for six or eight hours at the

least; a weighed portion of the solution was then evaporated to dryness, and the residue dried at a dull red heat. The numbers in the table indicate, in each instance, the proportion of anhydrous sulphate in 100 parts of water, free or combined, existing in the solution.

Temperature.	Anhydrous sulphate.	Sulphate with 2 atoms of water.	Sulphate crystallized in the cold.
12° C.	43·1	—	—
14	39·3*	—	—
18	25·8	16·4	—
19	—	—	11·7
25	20·6	—	—
38	13·0	—	—
40	—	—	8·8
50	11·0	—	6·5
100	—	—	1·7

The sulphate with 2 atoms of water does not attain its maximum of solubility till after a considerable time. Thus, at the temperature of 18°, the quantity of this salt dissolved in 100 parts of water was 13 after twenty-four hours, and 16·4 at the end of another day. This solution having been concentrated by evaporation *in vacuo*, till the greater part of the salt had separated out in crystals, the mother-liquor was found to contain 34 parts of the salt in 100. This salt appears thus to attain the solubility of the anhydrous sulphate. Moreover, the crystals which had formed were those of the hydrate with $\frac{8}{3}$ atoms of water.

Sulphate of didymium withstands a dull red heat, but is decomposed at a white heat. It is not completely decomposed by the heat of a spirit-lamp. A portion of anhydrous sulphate ignited for an hour in an intense charcoal fire lost 28·03 per cent of its weight, which is equivalent to 67·28 per cent, or nearly $\frac{2}{3}$ of the total quantity of sulphuric acid contained in it. In this manner the sub-sulphate, 3 DiO, SO_3, is obtained. It is a dull white powder, quite insoluble in water, either at ordinary temperatures or at the boiling-point. It dissolves but slowly in hydrochloric acid, even with the aid of ebullition, but dissolves readily in strong acids.

In another experiment, in which the ignition was not so strong, the loss of weight was only 17·5 per cent. The product treated with water separated into the soluble neutral sulphate and the insoluble sub-sulphate, exactly in the proportion indicated by this loss—a fact which demonstrates the actual existence of this tribasic sulphate.

Sulphate of Didymium and Ammonium.—On mixing the solutions of sulphate of didymium and sulphate of ammonia, there is formed,

* This number is probably too high, the solution not having been kept at that temperature for more than half an hour.

sooner or later according to the degree of concentration, a crystalline precipitate of a pale rose colour. This double sulphate dissolves in 18 times its weight of water, and is somewhat less soluble in a saturated solution of sulphate of ammonia.

Ignition at a dull red heat converts it into neutral sulphate of didymium, from the proportion of which, and that of the total amount of sulphuric acid, the composition of the salt may be determined:

		Calculated.	Found.
$3\,DiO$	168	39·44	39·34
NH_4O	18	6·10	6·25
$4\,SO_3$	160	37·56	37·71
$8\,HO$	72	16·90	16·70
$NH_4O, SO_3 + 3\,(DiO, SO_3) + 8\,Aq.$.	418	100·00	100·00

Of the 8 atoms of water, 6 atoms are driven off at 100°. The salt is not altered in composition by washing it till half is dissolved.

Sulphate of Didymium and Sodium.—A mixture of sulphate of didymium and sulphate of soda produces almost immediately, a pulverulent white precipitate, tinged with rose colour, which requires about 200 times its weight of water to dissolve it. In a solution of sulphate of soda it is still less soluble. Its very slight solubility renders it possible to determine its composition by synthesis. When the two salts were mixed in the proportion of 100 parts of sulphate of didymium to 37 of sulphate of soda, or 2 atoms of the former to 1 atom of the latter, the liquid, on being left to clarify and then decanted, still yielded a copious precipitate on the addition of a fresh portion of sulphate of didymium. But when the salts were mixed in the proportion of 25 parts (1 atom) of sulphate of soda to 100 parts (3 atoms) of sulphate of didymium, the clarified liquor gave no further precipitate with either salt. Hence the composition of the double salt is:

$$NaO, SO_3 + 3\,(DiO, SO_3),$$

a result which is confirmed by analysis:

		Calculated.	Found.	
$3\,DiO$ . . .	168	46·78	45·78	45·75
NaO . . .	31	8·67	—	—
$4\,SO_3$ . . .	160	44·55	45·78	45·13
	359	100·00		

The salt with which the analyses were made, had been calcined. The crystallized salt contains water; but different samples gave

different quantities, doubtless because they had not been prepared under the same conditions of temperature.

Sulphate of Didymium and Potassium.—On mixing the solutions of sulphate of didymium and sulphate of potash, there is immediately produced, if the solutions are somewhat concentrated, and especially if the latter salt is in excess, a white pulverulent precipitate. It afterwards goes on forming slowly, assuming a more granular and crystalline texture and a deeper rose colour. This double salt is much more soluble than the corresponding soda-compound, dissolving in 63 times its weight of water.

The two sulphates appear to unite in more than one proportion; but the most stable compound appears to be that which corresponds to the sodium-salt, viz.:

$$KO, SO_3 + 3\,(DiO, SO_3).$$

It appears also to contain 2 atoms of water.

Oxalate of Didymium.—This salt, when precipitated from neutral liquids, is pulverulent and of a white colour, slightly tinged with rose; when redissolved by heat in an excess of nitric or hydrochloric acid, it separates, on cooling, in a granular and crystalline form, sometimes even in small rose-coloured crystals, having the form of rectangular prisms, terminated by a pyramid with four faces placed upon the angles of the prism. This salt is perfectly insoluble in water, nearly insoluble in oxalic acid and in dilute mineral acids.

After drying in the air, it leaves, by roasting and calcination, between 44 and 45 per cent of oxide of didymium, and gives off about 20 per cent of water at 100°, but the diminution of weight goes on for several days. The oxalate dried at 100° leaves 55·53 per cent of oxide of didymium. Hence it appears that the salt contains 4 atoms of water, 3 of which go off at 100°.

DiO	. .	56	43·75	DiO	. .	56	55·45
C_2O_3	. .	36	28·12	C_2O_3	. .	36	35·64
4 HO	. .	36	28·13	HO	. .	9	8·91
$DiO, C_2O_3 + 4Aq$	.	128	100·00	$DiO, CO_3 + Aq$		101	100·00

The author concludes his paper with the following remarks:

"During the whole of this research, I was pre-occupied with the idea that the oxide whose combinations I was examining, might be not a simple oxide, but a mixture of two oxides, one of which might possibly be that of lanthanum. I therefore attended, as minutely as possible to the circumstances which might confirm that supposition. I have, however, met with only two facts, which may to a certain extent confirm this suspicion, viz.: 1. The scarcely perceptible increase of weight produced by the peroxidation of

oxide of didymium, an anomaly which is most easily explained by supposing that this peroxidation affects but a small portion of the mass; and, 2. The anomalous proportion of water in crystallized sulphate of didymium, which might lead to the supposition that this salt is a mixture of two salts with different degrees of hydration; it is, however, difficult to admit such a supposition with regard to very distinct and well-formed crystals, selected out of a number."

"On the other hand, I tried a great number of experiments with the view of demonstrating the existence of two different oxides, if they had been really present, but without any positive result. Thus, I compared attentively the series of precipitates produced by adding ammonia in successive portions to a didymic salt—the series of insoluble residues obtained by decomposing the nitrate or chloride by heat and digesting in water, a considerable number of times in succession—also the series of solutions obtained by successively treating the oxide, peroxide, sulphide, or oxysulphide with portions of dilute acid, not sufficient to dissolve it completely; but I have never observed any difference between the products obtained at the beginning and end of either of these series of operations. Neither was any particular result obtained by the action of chlorine on oxide of didymium suspended in water. The hydrate dissolves readily, preserving its aspect unaltered to the last; the peroxide likewise dissolves, though more slowly; and the part which dissolves last, does not differ in any respect from that which is first attacked."

"Thus, in spite of the considerations above adduced, I think it must be admitted that, although my oxide of didymium may have contained some traces of oxide of lanthanum, not completely eliminated by the crystallization of the sulphate, it was nevertheless essentially composed of one oxide, whose properties were not sensibly modified by the slight impurity just mentioned."

Researches on the Cinchona Alkaloïds,

By L. Pasteur.*

It is now about half a century, since *Cinchonine*, whose existence had been previously pointed out by Dr. Duncan, of Edinburgh, was first isolated and obtained in a state of purity, by Gomez, a physician of Lisbon. He attributed the efficacy of cinchona-barks to the presence of this body; but he failed to recognize its alkaline character, which, indeed, was not fully appreciated till towards the year 1820, by Pelletier and Caventou, at which time the same chemists likewise made the important discovery of *Quinine*. About twelve years

* Compt. Rend. XXXVII, 110.

later, two other French chemists, MM. Henry and Delohdre, discovered, in yellow cinchona-bark, a third alkaloïd to which they gave the name of *Quinidine*. In 1829, Sertürner, already celebrated by his discovery of morphine, observed in the mother-liquors of sulphate of quinine, an uncrystallizable base which he called *Quinoïdine*, and to which he attributed wonderful febrifuge properties.

The general characters of quinine and cinchonine are sufficiently well known; but with regard to quinidine and quinoïdine, very contradictory opinions still prevail. I think that I have removed all these difficulties. The results of my investigations likewise exhibit entirely new molecular relations between the several cinchona-alkaloïds. The following are the new facts which I have discovered.

1. *Cinchonicine*.—When cinchonine, in any of its salts, is subjected to the action of heat, it becomes transformed into a new base isomeric with it, but possessing totally different characters. This new base I call *Cinchonicine*. Any salt of cinchonine may be used for the preparation of cinchonicine; but to render the transformation easy and complete, and prevent it from going too far, the salt of cinchonine must be placed under certain conditions. In general, when a cinchonine-salt is heated, it immediately melts and decomposes; and if, by any particular artifice, we cause it to melt at a temperature considerably below that at which it decomposes, cinchonicine is produced; but if the heat be too strong, the new alkali is destroyed. Ordinary sulphate of cinchonine, for example, when directly heated, melts, and then immediately suffers decomposition, and is converted into a resinous substance of a fine red colour, which is a product of the transformation of the cinchonine. But if the sulphate, before it is heated, be mixed with a small quantity of water and sulphuric acid, it remains melted at a low temperature, even after all the water has been expelled, and if it be kept in this state for three or four hours, between 120° and 130°, it changes completely into sulphate of cinchonicine. The quantity of colouring matter formed is extremely small, indeed almost imponderable.

I prove, by facts which will be admitted by all chemists, that though heat plays an important part in this transformation of cinchonine, the vitreous, resinoïdal state of the product has nevertheless a real influence upon it; and that the isomerism of this base with cinchonine is due to transformations of the same kind that we meet with so frequently in Mineral Chemistry, as in soft sulphur, red phosphorus, and vitreous arsenious acid.

2. *Quinicine*.—All that has been said about cinchonine is applicable word for word, to the salts of quinine. When any salt of this base is heated, a new alkaloïd is formed isomeric with it. The conditions necessary and sufficient for ensuring this transformation are the same as those above indicated in the case of cinchonine. To the new base

I give the name of *Quinicine*. The best mode of obtaining it is to add a small quantity of water and sulphuric acid to commercial sulphate of quinine, and apply a moderate heat. The mass remains liquid even after the water has been completely expelled, and by continuing to heat it for four hours in an oil-bath to a temperature between 120° and 130°, the entire mass may be transformed into sulphate of quinicine, an extremely small quantity of colouring matter being formed at the same time.

In their general properties, cinchonicine and quinicine exhibit well-marked resemblances to the isomeric bases from which they are derived. They, moreover, resemble each other in the closest manner. Both are nearly insoluble in water, but very soluble in alcohol, whether absolute or of ordinary strength. Both of them unite readily with carbonic acid, and expel ammonia from its salts at ordinary tem peratures. Both are precipitated from their solutions in the form of resinous liquids, just like quinine under certain circumstances. Finally, both of them turn the plane of polarization to the right. They are equally bitter, and possess equal febrifugal powers.

3. *Quinidine*.—Allusion has already been made to the contradictions which are met with in the results of different chemists who have examined quinidine. All these contradictions may be attributed to a fact which has escaped the notice of former observers—viz.: that the name of quinidine has hitherto been applied indiscriminately to two alkaloïds which are totally distinct in their physical and chemical properties, and are almost always mixed together in the quinidine of commerce, unless care has been taken to purify it by several successive crystallizations. Thus, the quinidine discovered in 1833 by Henry and Delohdre is totally different from the substance at present known by that name in France and Germany; and the German product often contains a considerable quantity of that which was discovered by Henry and Delohdre. The leading characters by which these two alkaloïds may be distinguished from one another are the following: One of them, for which I shall retain the name of quinidine, is hydrated, efflorescent, *isomeric with quinine*, turns the plane of polarization to the right, and like quinine, acquires a green colour by the successive addition of chlorine and of ammonia. The other base, to which I give the name of *cinchonidine*, is anhydrous, *isomeric with cinchonine*, turns the plane of polarization to the left, and does not exhibit any green colouring under the circumstances just mentioned. It is this alkaloïd which is most abundant in the samples at present met with in commerce. By exposing recently crystallized cinchonidine to warm air, it is very easy to see whether it contains any quinidine, All the quinidine-crystals effloresce rapidly but without change of form. and separate with a dull white colour from the crystals of cinchonine, which retain their transparency. The green colouring by chlorine and ammonia likewise affords a useful test.

It appears, then, that the principal bases contained in cinchona-barks are four in number—namely, quinine, quinidine, cinchonine, and cinchonidine.

4. *Action of Heat on Quinidine and Cinchonidine.*—These two bases, when subjected to the action of a moderate heat, undergo exactly the same transformations as quinine and cinchonine—that is to say, *quinidine*, like quinine, is converted into *quinicine*, and *cinchonidine*, like cinchonine, into *cinchonicine*, the conditions necessary for the transformation being exactly the same as those already mentioned.

The molecular relations indicated by these results assume a new character when we compare the rotatory powers of the six alkalies. Consider, in the first place, the three isomeric bodies—quinine, quinidine, and quinicine. Quinine turns the plane of polarization to the left, quinidine to the right, and both to a considerable extent. Quinicine also turns it to the right, but very feebly as compared with the other two. Similarly with cinchonine, cinchonidine, and cinchonicine. Cinchonine and cinchonidine turn the plane of polarization, the one to the right, the other to the left, and both to a considerable amount; cinchonicine turns it very slightly to the right. The most rational, or rather the necessary, interpretation of these results appears to be as follows:—The molecule of quinine is double, consisting of two active bodies, one of which turns the plane of polarization considerably to the left, the other very slightly to the right. The latter is stable under the influence of heat, and does not undergo any isomeric transformation; but remaining without alteration in quinicine, gives to that body its feeble power of rotation to the right. The other group, which, on the contrary, is very active, becomes inactive when the quinine is heated, and therefore transformed into quinicine. Quinicine, therefore, is quinine, in which one of the constituent groups has become inactive. Quinicine may also be quinidine in which one of the constituent groups has become inactive; but in quinidine, this very active group turns the plane to the right, instead of to the left, as in quinine, and is, in the same manner, united with the same feeble and instable group possessing right rotatory power, which remains unaltered in quinicine, and gives to it its feeble rotatory power in that direction. All these observations might be repeated, word for word, with regard to cinchonine, cinchonidine, and cinchonicine, which, in fact, are constituted exactly like their three congeners, for they exhibit precisely the same relations.

5. *Quinoïdine.*—This body is always a product of transformation of the cinchona-alkalies. It originates in two different ways. It is produced in the preparation of sulphate of quinine, and especially in the American forests, when the woodman, after having stripped the bark from the tree, exposes it to the sun to dry it. The salts of

quinine, cinchonine, &c., contained in these barks are then transformed into resinous and colouring matters, which constitute the principal part of the quinoïdine of commerce. In fact, when any salt of quinine or cinchonine, either in dilute or concentrated solution, is exposed to the sun, even for a few hours only, it undergoes such a degree of alteration, that the liquid assumes a very deep red-brown colour. Further, this alteration is the same as that which takes place at a high temperature. I am, therefore, of opinion that in the preparation of quinine, cinchonine, &c., serious loss might be avoided, and the extraction of the alkalies greatly facilitated, if the cinchona barks were protected from light as soon as they are removed from the trees, and kept in the dark while they are drying. The manufacturer of quinine should carefully avoid the action of a strong light.

Transformation of the two kinds of Tartaric Acid into Racemic Acid. Discovery of inactive Tartaric Acid. New Method of separating Racemic Acid into the two Tartaric Acids, Right and Left.

By L. Pasteur.*

If, in examining the isomeric transformations of the alkaloïds mentioned in the preceding Memoir, we make use of the tartrates of those bases, and continue the action of the heat beyond the point at which cinchonicine and quinicine are formed, the modifying influence then extends to the tartaric acid itself. Thus, tartrate of cinchonine exposed to a gradually increasing heat, is first converted into tartrate of cinchonicine. But if the heat be continued, the cinchonicine becomes altered; it loses water, becomes coloured, and changes into quinoidine. At the same time, the tartaric acid likewise undergoes important modifications; and after five or six hours' exposure to a temperature of 170°, part of it is found to be converted into racemic acid. The tube must then be broken, the black resinous mass contained in it repeatedly treated with boiling water, the liquid filtered when cold, and mixed with excess of chloride of calcium. The whole of the racemic acid is then completely precipitated in the form of racemate of lime, whence it is easy to obtain the racemic acid itself.

The principal use of the cinchonine in this operation, is to impart a certain degree of stability to the tartaric acid, and enable it to bear, without destruction, a temperature which would alter it rapidly if it were in the free state. The transformation of the tartaric acid does

* Compt. Rend. XXXVII, 162.

not in any way depend upon the action exerted by cinchonine and cinchonicine upon polarized light. Tartaric ether—a compound in which tartaric acid is united to a substance which has no action on polarized light, but which can support a high temperature without destruction—yields, when subjected to the action of heat, a considerable quantity of racemic acid.

Racemic acid, thus artificially formed, is perfectly identical in all its physical and chemical properties with natural racemic acid. It possesses, in particular, this important character, of being resolvable into dextro-tartaric and lævo-tartaric acid, exhibiting equal and opposite rotatory powers in their combinations with bases.

This resolution of artificial racemic acid into dextro- and lævo-tartaric acids, leads to this consequence: that ordinary dextro-tartaric acid may be artificially transformed into its opposite—viz., lævo-tartaric acid; a consequence which is highly remarkable, especially when viewed in connection with the extraordinary fact, which will doubtless be explained at some future time, that we have never, by starting from an inactive body of any kind whatever, succeeded in producing a substance which acts upon polarized light; whereas nearly all the substances elaborated by nature in the vegetable organism are unsymmetrical, like tartaric acid.

This transformation of dextro-tartaric acid into racemic acid is rendered still more remarkable by the fact that lævo-tartaric acid may be converted into racemic acid under precisely similar circumstances. What a strange aptitude is revealed by these natural organic compounds! A group of unsymmetrical molecules, right and left, are, by the sole influence of a high temperature, half transformed into molecules of an opposite character, which, as soon as they are formed, unite with the former.

For a long time I regarded the production of racemic acid from tartaric acid as impossible. To this conclusion I was led by the following considerations: Racemic acid is a compound of dextro- and lævo-tartaric acids. The problem of transforming dextro-tartaric into racemic acid is the same as that of converting dextro-tartaric acid into lævo-tartaric. Now, all that can be done with the one acid may be done, under the same circumstances, with its opposite. If, therefore, any particular operation performed on the dextro-tartaric acid, converts it into lævo-tartaric, the same process applied to the latter should convert it into the former. The transformation appears, therefore, to be impossible. The utmost that we can hope to effect is the production of an inactive acid.

Happily, however, experiment has shown that these theoretical deductions were erroneous. Nevertheless, they have served me as a guide; and the less I was disposed to look for the transformation of tartaric acid into racemic, the more did I multiply my endeavours to discover inactive tartaric acid. Not only did the existence of this

latter appear possible from theoretical considerations, I was, moreover, aware of the intimate relation between tartaric and malic acid; and I had previously obtained inactive malic acid. Now, it was in looking for inactive tartaric acid, that I arrived at the formation of racemic acid. But, what is very remarkable—the very same operation yielded also considerable quantities of inactive tartaric acid. In other words, I obtained, together with racemic acid, a kind of tartaric acid which has no action whatever on polarized light, and is not resolvable, under the same circumstances as racemic acid, into dextro- and lævo-tartaric acid. This inactive tartaric acid is extremely curious; it crystallizes perfectly, and yields salts, which, for beauty of form, are not inferior either to the tartrates or to the racemates. I have already observed that, after treating with water the tartrate of cinchonine, which had been heated for several hours to 170°, and adding chloride of calcium, the racemic acid, formed at the expense of the tartaric, is precipitated in the form of racemate of lime. If now, the liquid be immediately filtered to remove the racemate, and then left at rest for twenty-four hours, an additional crop of crystals is obtained, consisting of pure inactive tartrate of lime, from which it is easy to obtain the inactive acid itself.

Lastly, I have ascertained that the inactive tartaric acid is produced in this operation at the expense of racemic acid previously formed. For if racemate of cinchonine be kept for some hours at 170°, a considerable portion is transformed into this same inactive tartaric acid.

Chemistry is now, therefore, in possession of four kinds of tartaric acid, viz.: Dextro-tartaric acid, lævo-tartaric acid, the compound of these two, viz.: racemic acid, and the inactive acid, which is neither right nor left, nor formed by the combination of the two. It is common tartaric acid *untwisted* (*détordu*) if I may use this expression, which roughly expresses my idea, and perhaps goes a little further—for we cannot be too cautious in the study of these difficult questions. Doubtless, this series of the four isomeric tartaric acids is a type, to which a large number of analogues will soon be discovered.

A serious difficulty may, however, be apprehended in the application of these new results. Thus, to pass from the right to the left term of the series, it is necessary to pass through racemic acid. Now what process have I given for the decomposition of racemic acid? It consists in the formation of the double racemate of soda and ammonia. The crystals obtained are of two kinds, which must be separated according to their hemihedric forms. In this process, however, there is no generality; the decomposition presents itself as an accident. It is certainly a very curious phenomenon, but we cannot assign any proximate cause for it; moreover, the sodio-ammoniac salt is the only one which exhibits this power of spontaneous decom-

position. Hence, it is very probable that in operating on bodies of any other series, we might obtain a substance analogous to racemic acid, but not possessing this power of decomposition, and consequently the inverse of the original compound might remain unknown. Such, indeed, was the state of the question not long ago; but I have recently discovered a process, not mechanical like that of the separation of the two kinds of tartaric acid in the crystals of racemate of soda and ammonia, but chemical, and depending on general principles.

I have, in fact, shown in a Memoir presented to the Academy a year ago, that the absolute identity of physical and chemical properties exhibited by right and left *symmetrical* bodies, no longer exists when then they are placed in contact with active bodies. Thus the dextro- and lævo-tartrates of the same active organic alkali differ altogether from one another in their crystalline forms, solubility, &c. It appeared, therefore, probable, that this dissimilarity might be made available for separating the two tartaric acids by whose union racemic acid is formed; and this result I have actually obtained, after many fruitless trials, by means of the two bases, quinicine and cinchonicine. Thus, in preparing the racemate of cinchonicine, it always happens that when the liquid has attained a certain degree of concentration, the first crop of crystals formed consists almost wholly of lævo-tartrate of cinchonicine, the dextro-tartrate remaining in the mother-liquid. A similar result is obtained with quinicine, excepting that in this case the dextro-tartrate crystallizes out first. Whenever, therefore, an organic compound is suspected to possess a binary constitution analogous to that of racemic acid, its resolution should be attempted by combining it with an active body, which, by the necessary dissimilarity of properties in the compounds which it is capable of forming with the constituents of the complex group, may afford the means of separating them.

We are now, then, in possession of general methods for converting a dextro-compound into its opposite and symmetric lævo-compound and likewise into the corresponding inactive body.

On the compounds of Glycerine with Acids, and on the synthesis of the proximate principles of Animal Fats.

By M. Berthelot.*

Glycerine, discovered in 1779 by Scheele, was at first regarded as a gummy substance peculiar to certain oils, and, in a certain sense, of accidental occurrence. The notions at present entertained on

* Compt. Rend. XXXVII, 398.

its nature and chemical functions are wholly due to Chevreul. This chemist in his "Recherches sur les Corps Gras," shows that a whole class of these bodies may be separated by the action of alkalies into two distinct parts, with fixation of water, viz., a fatty acid which unites with the alkali (forming soap) and glycerine. Hence have arisen two hypotheses. Either stearin, olein, butyrin, &c., are composed of oxygen, carbon, and hydrogen in such proportions that one part of their elements represents a fatty acid, either fixed or volatile, while the other portion, *plus* water, represents glycerine; or, these bodies, stearin, olein, &c., constitute a species of salts formed of an anhydrous fatty acid, fixed or volatile, and anhydrous glycerine—that is to say, their constitution is analogous to that of the ethers. Another group of fatty bodies contains cetine, which is characterized by the property of transforming itself into margaric and oleic acid, and ethal. The constitution of cetine gives rise to the same hypotheses.

The latter point of view has since been more and more developed and verified. Dumas and Péligot have confirmed the analogies of ethal and alcohol, first pointed out by Chevreul. They have formed with this body compounds similar to the ethers, or to cetine. Pélouze, on the other hand, has formed, with glycerine, the sulphoglyceric and phosphoglyceric acids, compounds analogous to the vinic acids; and in conjunction with Gélis, he has formed *butyrin*, the first neutral fatty matter that has been artificially obtained.

Berthelot has succeeded in generalizing these results, and in uniting glycerine both with the fatty acids, properly so called, and with other acids, organic and inorganic. The bodies thus formed are neutral, and incapable of combining with alkalies. Some are crystalline, others liquid.

They belong to several series. One of these series is identical with that of the natural fats; another, which is the more numerous, consists of bodies analogous to the ethers. Moreover, all these bodies may be represented in constitution by an acid, *plus* glycerine, *minus* water.

They all, when treated with alkalies, slowly reproduce the original acid and glycerine. Treated with concentrated hydrochloric acid, they decompose in the same manner. Treated with alcohol and hydrochloric acid, they give rise to a double decomposition, yielding glycerine, and an ether of the acid previously united with the glycerine. These two reactions they exhibit in common with the natural fats. Finally, ammonia converts them into amides.

When subjected to the action of heat, they decompose and yield acrolein, with the exception of two which are volatile. Nevertheless, stearin, olein, margarin, and palmitin, in very small quantities, may be distilled in the barometric vacuum without yielding acrolein or

turning acid. The same fact was observed by Chevreul with regard to the natural fats.

These various bodies are obtained by the direct union of their two proximate principles, the acid and glycerine. This union is produced by prolonged contact of the two bodies in close vessels, at a temperature more or less elevated. Nearly all of them form likewise at ordinary temperatures, but in very small quantity. In certain cases, they are obtained by double decomposition between the ethers and glycerine.

Lastly, they may be formed by the action of hydrochloric acid on the mixture of glycerine and the acid. It is worth while to remark the two opposite functions discharged by the hydrochloric acid; when dissolved in water, and added in large excess, it decomposes the neutral fats into glycerine and fatty acids; but when it acts in the form of gas on a mixture of syrupy glycerine and the acid, it causes the two bodies to combine.

These bodies may be divided into three groups—viz., 1. Compounds of glycerine with the fatty acids, properly so called (these combinations reproduce the fatty bodies which occur in the organic kingdom). 2. Compounds of glycerine with various organic acids, and not identical with any known compounds in the organic world. 3. Compounds of glycerine with mineral acids, likewise not identical with any known natural organic compound.

I.—COMPOUNDS OF GLYCERINE WITH THE FATTY ACIDS PROPERLY SO CALLED.

A.—*Fixed Fatty Acids.*

Stearin.—Stearic acid (melting at 70° C., prepared by Chevreul's method) forms with glycerine three compounds—viz., monostearin, distearin, and tetrastearin; the last of which is identical with natural stearin.

Monostearin $\left\{\begin{array}{l} C_{42}H_{42}O_8 = C_{36}H_{36}O_4 + C_6H_8O_6 - 2\,HO \\ C_{92}H_{163}O_{15} = C_{70}H_{139}O_7 + 2\,C_6H_{16}O_6 - 4\,H_2O \end{array}\right\}$

is obtained by heating a mixture of equal parts of glycerine and stearic acid to 200° for twenty-six hours. The glycerine and acid remain superposed without any appearance of dissolving one in the other. The neutral substance formed is likewise insoluble in the glycerine. After cooling, the solid stratum which floats on the excess of glycerine, is separated, fused, mixed with a small quantity of ether, then with slaked lime to separate the uncombined acid, and kept at 100° for a quarter of an hour. It is then exhausted with boiling ether (which does not separate stearic acid from lime under these circumstances). A white, neutral substance is thus obtained, very

slightly soluble in cold ether, and crystallizing in fine, double-refracting needles. These microscopic needles are usually grouped in rounded grains.

Monostearin melts at 61° and solidifies at 60°. It volatilizes without alteration in the barometric vacuum. Heated in the air, it begins to evaporate, and then decomposes with formation of acrolein. It burns with a white and very brilliant flame.

Treated with oxide of lead at 100°, it saponifies in a few hours, reproducing glycerine and stearic acid melting at 70°. The weight of glycerine thus reproduced amounts to nearly a fourth of that of the monostearin.

When kept for six hours at 100° in contact with strong hydrochloric acid, it is almost wholly resolved into glycerine and stearic acid. Acetic acid mixed with alcohol does not decompose it under the same circumstances. These various reactions are the same as those exhibited by natural stearin.

A similar compound is obtained by saturating with hydrochloric acid a mixture of syrupy glycerine and stearic acid at the temperature of 100°; but the compound thus formed melts at 47°, and is mixed with chlorhydrin, from which it cannot be separated.

A mixture of glycerine and stearic acid, kept at the ordinary temperature of the air, yield traces of a neutral crystalline fat.

Distearin $\left\{\begin{array}{l} C_{78}H_{78}O_{12}=2\,C_{36}H_{36}O_4+C_6H_8O_6-2\,HO \\ C_{76}H_{151}O_{11}=\ C_{70}H_{139}O_7+C_6H_{16}O_6-2\,H_2O \end{array}\right\}$

is obtained by heating a mixture of equal parts of glycerine and stearic acid to 100° for one hundred and fourteen hours. It is purified by lime and ether, like the preceding compound. It is white, neutral, granular, and when examined by the microscope appears to be composed of oblique, flattened, double refracting laminæ. It melts at 58°, and solidifies at 55°. Yields acrolein when heated. When treated with oxide of lead at 100°, it reproduces glycerine and stearic acid fusible at 70°.

The same substance may also be obtained, either by heating the stearoglyceric mixture to 275° for seven hours, or by heating a mixture of 1 part monostearin and 3 parts stearic acid to 270°, or by heating natural stearin to 200° for twenty-two hours with excess of glycerine.

Tetrastearin $\left\{\begin{array}{l} C_{150}H_{146}O_{16}=4\,C_{36}H_{36}O_4+C_6H_8O_6-6\,H\,O \\ C_{146}H_{282}O_{14}=2\,C_{70}H_{139}O_7+C_6H_{16}O_6-6\,H_2O \end{array}\right\}$

is obtained by heating monostearin to 270° for some hours, with fifteen or twenty times its weight of stearic acid. Water is eliminated, and condenses in the upper part of the tube. Combination does not take place by simple fusion; it requires time. This body is purified by lime and ether like the preceding.

Tetrastearin is neutral, and has the same composition as natural stearin.

2. *Margarins.*—Margaric acid (from human fat) forms with glycerine, two neutral compounds—viz., Monomargarin and Tetramargarin.

Monomargarin ($C_{40}H_{40}O_8 = C_{34}H_{34}O_4 + C_6H_8O_6 - 2\,HO$) is obtained either at 200° or at 100°. It is formed even at ordinary temperatures, but in very small quantity. Its formation is easier than that of any other solid fat. It melts at 56°, and solidifies at 49°. Treated with oxide of lead, it reproduces glycerine, and margaric acid melting at 60°. Its reactions are similar to those of stearin, excepting that, when heated to 100° for six hours with a mixture of alcohol and acetic acid, it is partially decomposed, yielding margaric acid and glycerine, a reaction not exhibited by stearin.

Tetramargarin appears to be formed by heating monomargarin to 100° with excess of margaric acid. It has not been obtained quite pure. When saponified, it yields margaric acid fusible at 60°, and glycerine.

It will be observed that the stearins, which are prepared with an acid melting at 70°, reproduce by saponification an acid which melts at 70°; whereas the margarins, prepared with an acid melting at 60°, reproduce by saponification an acid melting at 60°. This fact confirms the existence of stearic and margaric acids as distinct and permanent bodies.

3. *Palmitins.*—Palmitic acid forms with glycerine three compounds analogous to those produced by stearic acid, and obtained under similar circumstances.

Monopalmitin ($C_{38}H_{38}O_8 = C_{32}H_{32}O_4 + C_6H_8O_6 - 2\,HO$), melting at 58°, solidifying at 45°;

Dipalmitin ($C_{70}H_{70}O_4 = 2\,C_{32}H_{32}O_4 + C_6H_8O_6 - 2\,HO$), melting at 59°, solidifying at 51°; and

Tetrapalmitin ($C_{134}H_{130}O_{16} = 4\,C_{32}H_{32}O_4 + C_6H_8O_6 - 6\,HO$), melting at 60°, solidifying at 46°. This last is identical with natural palmitin.

All these three compounds, when treated with oxide of lead, reproduce glycerine, and palmitic acid melting at 61°. Monopalmitin treated with alcohol and acetic acid for one hundred and two hours at 100°, is decomposed with separation of glycerine, a property likewise exhibited by natural palmitin.

4. *Olein.*—Oleic acid (purified by twice filtering the commercial acid at a temperature near 0°, then converting it into oleate of baryta, and crystallizing that salt from alcohol) forms at 200° a neutral *Monolein* ($C_{42}H_{40}O_8 = C_{36}H_{34}O_4 + C_6H_8O_6 - 2\,HO$). This compound is an oily liquid, which solidifies at near 15°. Its density is 0·947. Oxide of lead saponifies it very slowly, and with difficulty.

Alcohol and acetic acid do not decompose it at 100°, in which respect it resembles natural olein.

This body is also formed by double decomposition, by heating to 100° a mixture of oleic ether, glycerine, and hydrochloric acid.

Diolein ($C_{78}H_{74}O_{12}=2C_{36}H_{34}O_4+C_6H_8O_6-2HO$) is obtained by heating natural olein with glycerine to 200° for twenty-two hours. Its density at 21° is 0·921. It begins to crystallize at 15°.

It is also obtained by heating monolein with oleic acid.

B.—*Volatile Fatty Acids.*

These acids likewise unite with glycerine, under the same conditions as other fixed acids, producing by direct combination, various liquid compounds, which are neutral and odoriferous. These liquids may be decomposed by alkalies, by hydrochloric acid, and even by acetic acid or water, into acids and glycerine. A mixture of alcohol and hydrochloric acid converts them into ethers and glycerine. Alcohol alone, in large quantity, suffices to commence this double decomposition, either at 100° in eighty-eight hours, or at the ordinary temperature with access of air.

These compounds are prepared by heating the mixture of an acid with glycerine, adding excess of carbonate of potash after the liquid has cooled, then agitating with ether, evaporating in the water-bath, and drying *in vacuo* with the aid of heat.

The mere contact of glycerine with a volatile fatty acid continued for three months, at the ordinary temperature, is sufficient to form the compound in considerable quantity, at least in the case of butyric acid.

These bodies are likewise formed by the action of hydrochloric acid gas, or a mixture of glycerine with the acid, or even of glycerine with the ether of the fatty acid.

1. *Valerins.*—The following have been obtained:

Monovalerin ($C_{16}H_{16}C_8=C_{10}H_{10}O_4+C_6H_8O_6-2HO$) at 200°, is a neutral, oily, odoriferous liquid, which has a density=1·100, and is slowly changed into valeramide by the action of ammonia.

Divalerin ($C_{26}H_{26}O_{12}=2C_{10}H_{10}O_4+C_6H_8O_6-2HO$) a neutral, oily liquid, having a disagreeable odour, a bitter, aromatic taste, a density of 1·059, is formed at 275°, by the action of the aqueous acid and glycerine.

2. *Butyrins.*—Butyric acid produces three compounds:

Monobutyrin ($C_{14}H_{14}O_8=C_8H_8O_4+C_6H_8O_6-2HO$) is a neutral, oily, odoriferous liquid, having a bitter and aromatic taste, and a density of 1·088; it is formed in presence of excess of glycerine, either at ordinary temperatures, or at 200°. When saponified by baryta, it yields half its weight of butyric acid.

Dibutyrin ($C_{22}H_{22}O_{12}=2C_8H_8O_4+C_6H_8O_6-2HO$) is a neutral, only liquid, having a density of 1·081, volatilizing towards 300°, without apparent decomposition, mixing with alcohol and ether, slightly soluble in water; it is formed either at 275° or at 200°, with the aqueous acid. When saponified by baryta, it yields $\frac{2}{3}$ of its weight of butyric acid.

Butyridin ($C_{14}H_{13}O_7=C_8H_8O_4+C_6H_8O_6-3HO$) is a neutral, oily liquid, having an unpleasant odour, of medium fluidity, density = 1·084, soluble to a considerable extent in a solution of carbonate of soda; it is formed by heating to 200° a mixture of 1 part of glycerine and 4 parts of butyric acid. When treated with ammonia, it changes in the course of five days into butyramide.

3. *Acetins.*—Acetic acid, which in this point of view may be regarded as a fatty acid, forms two compounds, viz:

Acetin ($C_{10}H_{10}O_8=C_4H_4O_4+C_6H_8O_6-2HO$), a neutral liquid, of slightly ethereal odour, density = 1·20; formed at 100°, and *Acetidin* ($C_{10}H_9O_7=C_4H_4O_4+C_6H_8O_6-3HO$), a neutral, odoriferous liquid, having a pungent taste, mixing with water, volatile at 280°, having a density = 1·184. It is formed under the most different circumstances, either at 275° or at 200°, in presence of excess of glycerine, or excess of acid, aqueous or not. When saponified by baryta, it yields glycerine, and half its weight of acetic acid.

II.—COMPOUNDS OF GLYCERINE WITH VARIOUS ORGANIC ACIDS.

Glycerine may be made to unite with benzoic, sebacic and camphoric acid, merely by the action of time and of heat.

Benzoycin ($C_{20}H_{12}O_8=C_{14}H_6O_4+C_6H_8O_6-2HO$) is a light-coloured, very viscid oil, nearly or quite inoxidable, of density 1·228; it is formed either at 200° or 270°, and may be purified in the same manner as butyrin. It begins to form at 100°, or even at the ordinary temperature, and is also produced by the action of hydrochloric acid on a mixture of glycerine and benzoic ether, or even by the direct action of glycerine in large quantity on benzoic ether at 100°. Alkalies convert it into benzoic acid and glycerin; alcohol and hydrochloric acid, into benzoic ether and glycerine; the same decomposition is likewise produced even by alcohol alone, when in large quantity, either at 100°, or at ordinary temperatures with access of air. Lastly, ammonia converts it into benzamide.

Sebin ($C_{32}H_{30}O_{10}=C_{20}H_{18}O_8+2C_6H_8O_6-4HO$) is obtained at 200°. It is a neutral, crystallizable body, resolved by oxide of lead into sebacic acid and glycerine.

Camphorin is neutral, viscid like thickened turpentine, soluble in ether, decomposable by oxide of lead into acid and glycerine.

III.—COMPOUNDS OF GLYCERINE WITH MINERAL ACIDS.

Chlorhydrin ($C_6 H_7 ClO_4 = C_6 H_8 O_6 + HCl - 2 HO$) is obtained by saturating glycerine at a gentle heat with hydrochloric acid gas, and keeping the solution at 100° for thirty-six hours. Without this precaution, only traces of the product are obtained. The solution is then saturated with carbonate of soda, agitated with ether, and the ether evaporated. The residue of this operation, when subjected to distillation, yields chlorhydrin at 227° (a fixed point). It must then be treated a second time with lime and ether. Chlorhydrin is a neutral oil, having a fresh and ethereal odour, a saccharine taste, with a pungent after-taste, and mixing with water and ether; its density is 1·31.

It does not precipitate nitrate of silver, at least not immediately. It burns with a white flame bordered with green, eliminating hydrochloric acid. Oxide of lead saponifies it slowly and with difficulty, yielding quantities of glycerine and hydrochloric acid, nearly proportional to the equivalents of those bodies.

The glyceric compounds prepared by the action of hydrochloric acid on glycerine and an acid, all contain chlorhydrin united, or we may say allied with them, and it cannot be separated from them completely.

Chlorhydrin is also formed, though merely as a trace, by the action of strong hydrochloric acid on the neutral fats.

On Propionic Alcohol.

By G. Chancel.

This alcohol, to which the author gives the name of *Hydrate of Trityl*, has been obtained from the residue of the distillation of *esprits de marcs*, a product which had been previously shown by Balard to consist of amylic alcohol. The first portions of the distillation of these residues were rectified several times, and purified by a method which will be described elsewhere. The product was agitated with carbonate of potash, to remove the greater part of the water, then left for twenty-four hours in contact with fused hydrate of potash, and distilled over that substance.

Hydrate of Trityl (which may also be called Propionic or Propylic Alcohol) contains:

$$C_6 H_8 O_2 = \left\{ \begin{matrix} C_6 H_7 \\ H \end{matrix} \right\} O_2;$$

It is a perfectly limpid liquid, lighter than water, and having a fruity, intoxicating odour. It is very soluble in water, though it does not dissolve in that liquid in all proportions. It boils at 96°.

Its vapour density = 2·02, corresponding to 2 vols. for the above formula. It unites readily with sulphuric acid.

Sulphotritylic Acid is obtained in the state of a potash-salt, by saturating with carbonate of potash, a mixture of sulphuric acid and hydrate of trityl diluted with water; evaporating to dryness over the water-bath; and exhausting the residue with boiling absolute alcohol, which dissolves the sulphotritylate of potash. This salt contains

$$C_6 H_7 KSO_4 = \left\{ \begin{matrix} C_6 H_7 \\ K \end{matrix} \right\} O, SO_3.$$

As the solution cools, the salt is deposited in delicate needles, very soluble in water and anhydrous.

Tritylo-sulphocarbonic Acid is likewise obtained in the form of a potash-salt, by dissolving caustic potash in hydrate of trityl, and adding sulphide of carbon to the solution. The salt is then deposited in slender needles.

Hydrate of trityl readily combines with other acids to form compound ethers.

This alcohol is probably not the only one which accompanies the hydrate of amyl in the *huiles de mare*. M. Faget is at present engaged in examining the less volatile portions, with the hope of discovering the higher homologues.

The formation of the different alcohols by the decomposition of sugar or glucose under the influence of ferments, may be represented by the following equations:

$$2\,C_{12}H_{12}O_{12} = 8\,CO_2 + 4\,C_4 H_6 O_2 \text{ hydrate of ethyl.}$$

$$\text{,,} = 8\,CO_2 + \left\{ \begin{matrix} C_4 H_6 O_2 \text{ hydrate of ethyl.} \\ 2\,C_6 H_8 O_2 \text{ hydrate of trityl.} \\ 2\,HO \end{matrix} \right.$$

$$\text{,,} = 8\,CO_2 + \left\{ \begin{matrix} 2\,C_8 H_{10} O_2 \text{ hydrate of tetryl.} \\ 4\,HO \end{matrix} \right.$$

$$\text{,,} = 8\,CO_2 + \left\{ \begin{matrix} C_6 H_8 O_2 \text{ hydrate of trityl.} \\ C_{10} H_{12} O_2 \text{ hydrate of amyl.} \\ 4\,HO \end{matrix} \right.$$

The last equation seems to show that the formation of hydrate of amyl is necessarily accompanied by that of hydrate of trityl.

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XXII.—*On two new methods for the determination of Nitrogen in organic and inorganic compounds.*

By Maxwell Simpson, M.D., Dublin, F.C.S.

Having been recently engaged in investigating the constitution of several interesting nitro-compounds, my progress was arrested by the difficulties I encountered in the determination of the amount of their nitrogen. In fact, all the methods of analysis at present known proved inapplicable. From the peculiarity of the constitution of these bodies, I could not with safety employ the soda-lime process. I had, therefore, recourse to Liebig's qualitative method, but totally failed, in consequence of oxide of copper being incapable of effecting complete combustion of these compounds, they being remarkably rich in carbon. I did not try Dumas' or Bunsen's method, as the same source of failure obviously exists in both.

With a view of removing this difficulty, and at the same time of supplying a want which has been long felt in organic chemistry, I commenced the present research, which has for its object the discovery of a new method for the determination of nitrogen, which shall be easy of execution, accurate, and at the same time general in its application.

The methods I am about to describe will, I have no doubt, be found applicable to the analysis of almost all nitrogenous compounds, whether organic or inorganic. The first, which is a comparative method, may be employed for the analysis of those bodies in which the amount of the nitrogen bears a considerable proportion to that

of the carbon. Bodies containing 1 equivalent of nitrogen to 10 or even 15 equivalents of carbon, may be safely analysed according to this process. The second, which is an absolute method, is applicable to the analysis of almost all substances, whether rich or poor in nitrogen.

COMPARATIVE METHOD.

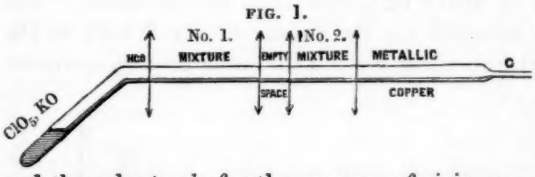
The principle of this method is the same as that of Liebig's. The organic substance is burnt, and the evolved gases, namely, carbonic acid and nitrogen, are collected in a graduated tube over mercury, and their relative proportion ascertained by absorbing the former by means of caustic potash. The combustion of the organic compound is, however, effected by means of oxide of mercury instead of oxide of copper. The employment of the former as the agent of combustion involves the necessity of using a large quantity of metallic copper in the fore-part of the combustion-tube, to absorb the free oxygen, which would otherwise enter the graduated jar and vitiate the analysis. No explosion is to be apprehended, as the oxygen in the combustion-tube is largely diluted with mercurial vapour. It is of course necessary in this, as in Liebig's process, that the amount of carbon in the substance intended for analysis should have been previously determined.

It is indispensable to the success of this method, that all the substances employed in it should not only be free from nitrogen, but from all bodies capable of absorbing carbonic acid, such as potash, baryta, &c. Now as the red precipitate of commerce is frequently contaminated with nitric acid, it is quite inapplicable; it therefore becomes necessary to prepare it specially for the process. The following is the best manner of preparing it.

A solution of corrosive sublimate is treated with an excess of caustic potash (an excess is necessary, in order to prevent the precipitation of an oxychloride), and the precipitate, which is thrown down, is washed by decantation till the supernatant liquor ceases to turn red litmus blue. It is next transferred to an evaporating basin, the liquor removed by a pipette, and a solution of phosphoric acid added, drop by drop, till the moist mass acquires a distinctly acid reaction, and retains it even after stirring. Finally the mercury is dried, heated pretty strongly, and preserved in a well-stoppered bottle for use. The addition of phosphoric acid effectually secures the absence of free potash. It is advisable to prepare it by burning a little phosphorus under a bell-jar. I shall now describe the process in detail.

A narrow combustion-tube, of hard and tolerably thick Bohemian glass, 32 inches in length, is selected and sealed at one end. A quantity of chlorate of potash, about 8 or 9 grms., which has been previously fused and powdered, is now introduced, and about 3 inches beyond it, the tube is bent into an obtuse angle, as represented in Fig. 1. A plug of freshly ignited asbestos is driven up to this angle, which it should fit pretty tightly and yet permit the passage of gas. The interval between the chlorate and the asbestos is for the purpose of giving room for the frothing up of the former on the application of heat. Two grammes of oxide of mercury are next added, and then a second asbestos plug. One decigramme of the substance intended for analysis is weighed out, and intimately mixed with $4\frac{1}{2}$ grms. of oxide of mercury and $1\frac{1}{2}$ grms. of oxide of copper.* The copper is employed simply to dilute the mixture and to make up for defective mixing, as the above quantity of oxide of mercury is quite sufficient for the complete combustion of 1 decigramme of any organic substance. This mixture is transferred to the tube, and so disposed as to form a stratum of 6 or 7 inches in length.

FIG. 1.



An asbestos plug is now introduced, and then a second, distant about 2 inches from the first, an empty space being left between the two as shown in Fig. 1. A second organic mixture is next formed, composed of 3 grms. of oxide of mercury, 1 grm. of oxide of copper, and 0·07 grm. of substance, which is also transferred to the tube and arranged so as to occupy about 4 inches of it. A quantity of finely-divided metallic copper, about 8 or 10 grms., is finally placed in the fore-part of the tube, a little asbestos separating it from the organic mixture, and spread out so as to form a thin layer, of about 6 or 7 inches in length.† The tube being thus filled, is drawn out in front about 2 or 3 inches, and a gas-delivery tube, having the form

* I would strongly recommend the employment of a mixture of equal parts of oxide of copper and oxide of mercury for the determination of carbon in graphite, carburets of iron, albumen, and other substances difficult of combustion. Liebig's apparatus for organic analysis may be employed without modification. The determination of the hydrogen must, however, be given up, as mercurial vapour would condense in the chloride of calcium, and increase its weight.

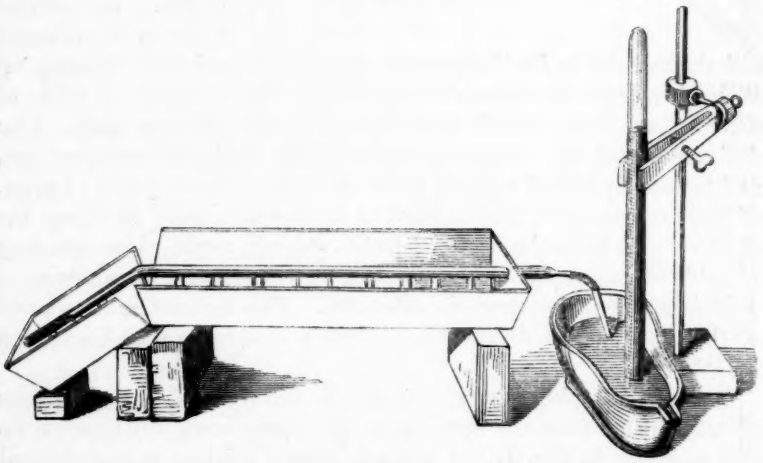
† The copper is best prepared by reducing oxide of copper by means of hydrogen gas. If the reduction be effected at a low temperature, the copper is obtained in a very minute state of division, and is admirably fitted for the absorption of oxygen.

represented in Fig. 2, is attached to it by means of a caoutchouc joint.

FIG. 2.

Two combustion-furnaces are now arranged in such a manner as to form an obtuse angle with each other, as represented in Fig. 3. An old furnace may be made to answer remarkably well, if it be cut across, at a distance of about 12 inches from the extremity. The tube is arranged on the furnaces with 1 inch of the wide part projecting beyond the anterior one, as shown

FIG. 3.



in the drawing. This is necessary for the preservation of the caoutchouc connector, as the narrow part of the tube with which it is in contact becomes highly heated during the combustion, from the condensation in it of a large quantity of mercurial vapour.

The delivery-tube is now plunged beneath the surface of mercury in a mercurial trough, and heat is cautiously applied to the chlorate, so as to produce a rapid but not tumultuous evolution of gas (*See* Fig. 3). When the transmission of gas has proceeded for a short time, it is advisable to heat gently the unmixed oxide of mercury at the angle of the tube, so as to produce a slight disengagement of oxygen, and thereby more completely to remove the atmospheric air mechanically retained in its pores. When the chlorate is nearly exhausted, the tube is heated to redness from its sealed extremity to its angle, and maintained at a red heat during the entire process, in order to prevent products of decomposition distilling back into this part, on the application of heat to the organic mixture.

Having thus driven the atmospheric air completely out of the tube and replaced it by oxygen, the next step is to burn the organic mixture No. 2, and allow the gaseous products to escape through the mercury into the air without being collected. The object of this will be afterwards explained. The combustion is conducted in the following manner.

The empty space (Fig. 1), which must be shaded by an iron screen at each end, in order to prevent the heat from extending to the organic mixtures, is heated first, and afterwards the metallic copper. The latter is quickly raised to a full red heat, and as soon as the mercury is observed to rise in the delivery-tube, from the absorption of oxygen by the copper, a small quantity of the mixture No. 2 is heated, beginning with the anterior part, the rest being protected by a screen. The combustion of the entire mixture is proceeded with by gradually shifting back the screen and exposing a small quantity of it at a time to the action of the fire. The empty space as well as the metallic copper must be maintained at a full red heat during the entire combustion. The object of heating the former is to prevent products of decomposition, on the application of heat to the mixture No. 2, from distilling back to mixture No. 1, which products might differ from the original substance in the relative proportion of their carbon and nitrogen.

We have thus, by the burning of the anterior mixture, removed the oxygen from that part of the combustion-tube which is in front of the metallic copper, and from the delivery-tube (the oxygen behind the copper does not interfere with the process, as it cannot pass the red-hot metal), and replaced it by a gaseous mixture of the same composition as that which the combustion of the posterior mixture will afford. The tube being now in a proper condition, the fire may be extended to mixture No. 1 (Fig. 1), and the gaseous products may now be collected. This is done in the following manner.

A eudiometer is filled with mercury, and all air-bubbles having been carefully removed, it is inverted and plunged beneath the surface of the mercury in the trough, and as soon as the evolution of gas from mixture No. 2 has ceased, the delivery-tube is brought under it, and the combustion of mixture No. 1 is commenced, (Fig. 3). Before filling the eudiometer, it is necessary to moisten the inside with a drop of water, in order that the gas afterwards to be collected in it may be saturated with moisture, a condition requisite for its accurate measurement. An ordinary Bunsen's eudiometer will answer very well, provided it possess the necessary capacity. The

tube I usually employed was 550 millimetres in length, had an internal diameter of 21 millimetres and a capacity of about 200 cubic centimetres. This I found quite large enough to contain the products of combustion from 1 decigramme of substance. It is of course not necessary that it should be provided with platinum wires. For the method of constructing and graduating a eudiometer, I must refer to the "Handwörterbuch der Chemie," vol. II, p. 1053.

The eudiometer being placed on the delivery-tube, the combustion of mixture No. 1 is commenced, and so conducted as to produce a slow but uninterrupted evolution of gas. As soon as the combustion is terminated, heat is applied to the unmixed oxide of mercury at the angle of the tube, in order that the oxygen evolved may drive the last portions of gas into the eudiometer. When the operation is at an end, the eudiometer is disconnected and transferred to a mercurial trough with glass sides.

At the expiration of six or seven hours, the volume of gas is read off and properly corrected for temperature and aqueous vapour. An observation cannot with safety be made sooner, since both the gas and the column of mercury in the eudiometer (which must be afterwards compared with a cold barometric column) acquire a very high temperature during the combustion, in consequence of their proximity to the furnace. A potash ball, attached to a platinum wire, is now moistened with water and introduced into the eudiometer. It should be made in such a manner as to contain as much water of crystallization as possible in addition to its basic water.* As soon as the absorption of the carbonic acid is complete and the residual nitrogen quite dry, the ball is withdrawn and a second observation is made. This corrected for temperature and pressure, gives the nitrogen, and the difference between this and the first gives the carbonic acid.

The advantages which this method offers are:

1st. Complete combustion of the organic substance is secured, as it is burnt in an atmosphere of oxygen gas.

2nd. The formation of all oxides of nitrogen is entirely prevented, by the incandescent mercurial vapour with which the tube is filled during the combustion.

3rd. From the method of the analysis we are enabled to collect almost the whole of the gas evolved in the combustion of the posterior organic mixture, so that the carbon and nitrogen might be almost quantitatively estimated. It is true, that at the termination of the combustion, a small quantity of gas remained in the delivery-tube,

* Handwörterbuch, II, 1063.

which could not be driven into the eudiometer by the oxygen; but this is compensated by the delivery-tube having been full of gas from the anterior mixture, when the combustion of the posterior one was commenced, which was of course driven into the eudiometer.

Should the operator apprehend that oxygen has passed into the eudiometer, he can at once satisfy himself on this point by examining the tube after the combustion. In a well-conducted analysis, there will always be 2 or 3 inches of perfectly bright metallic copper in the fore-part of the tube.

I shall now give the results of the analyses that were made, in order to test the accuracy of this method. The substances employed were all obtained from Merck's establishment in Darmstadt, and were remarkably pure.

URIC ACID.

	Observed vol.	Temp. C.	Height of mercury above that in trough.	Barom.	Corrected vol. at 0° C. and 1mm pressure.
Vol. of mixed gases CO_2 + N (moist)	471·05	17·3°	117·0mm	743·3mm	270·94
After absorption of CO_2 (dry) . .	219·54	17·2°	363·4 „	742·4 „	78·27

Relation by volume.

Theory 2·5 C. : 1·000 N.
Experiment 2·5 „ : 1·015 „

CAFFEINE I.

	Observed vol.	Temp. C.	Height of mercury above that in trough.	Barom.	Corrected vol. at 0° C. and 1mm pressure.
Vol. of mixed gases CO_2 + N (moist)	489·28	18·5°	103·7mm	740·0mm	284·32
After absorption of CO_2 (dry) . .	183·62	18·5°	403·1 „	738·3 „	57·64

Relation by volume.

Theory 4 C. : 1·000 N.
Experiment 4 „ : 1·017 „

CAFFEINE II.

	Observed vol.	Temp. C.	Height of mercury above that in trough.	Barom.	Corrected vol. at 0° C. and 1mm pressure.
Vol. of mixed gases CO_2 + N (moist)	406·98	19·1	149·3mm	743·2mm	219·65
After absorption of CO_2 (dry) . .	141·95	18·7	411·4 „	745·8 „	44·42

Relation by volume.

Theory 4 C. : 1·000 N.
Experiment 4 „ : 1·014 „

ASPARAGIN.

	Observed vol.	Temp. C.	Height of mercury above that in trough.	Barom.	Corrected vol. at 0° C. and 1mm pressure.
Vol. of mixed gases $CO_2 + N$ (moist)	347·15	18·9	194·7mm	743·2mm	172·82
After absorption of CO_2 (dry) . .	110·49	19·5	407·9 „	741·4 „	34·58

Relation by volume.

Theory 4 C. : 1.000 N.
Experiment 4 „ : 1·0007 „

HIPPURIC ACID.

	Observed vol.	Temp. C.	Height of mercury above that in trough.	Barom.	Corrected vol. at 0° C. and 1mm pressure.
Vol. of mixed gases $CO_2 + N$ (moist)	423·24	19 4	124·4mm	736·7mm	235·35
After absorption of CO_2 (dry) . .	54·7	19·4	485·4 „	736·3 „	12·81

Relation by volume.

Theory 18 C. : 1·000 N.
Experiment 18 „ : 1·036 „

QUININE.

	Observed vol.	Temp. C.	Height of mercury above that in trough.	Barom.	Corrected vol. at 0° C. and 1mm pressure.
Vol. of mixed gases $CO_2 + N$ (moist)	441·18	17·5	112·9mm	739·7mm	253·78
After absorption of CO_2 (dry) . .	55·9	18·4	493·4 „	741·9 „	13·01

Formula.	Relation by volume.
$C_{28} H_{22} N_2 O_4$) Theory	19 C. : 1·000 N.
(Laurent's)) Experiment	19 „ : 1·027 „

The method I have just described is proposed as one remarkably easy of execution, and sufficiently accurate for the analysis of compounds rich in nitrogen. Indeed, greater accuracy cannot be attained by Dumas' absolute method, in which from 3 to 6 decigrammes of substance are employed, and all the trouble of drying and accurately weighing it must be gone through.* The error in all these analyses, it will be observed, is always in the same direction, and may with perfect safety be taken into account in all results obtained by this method.

The sources of inaccuracy are:

1st. Air adheres with great obstinacy to the oxide of mercury in

* Handbuch der Analytischen Chemie, von Rose, II, 814.

the combustion-tube, and cannot be entirely removed, even by a protracted transmission of gas. From the method of the analysis, however, it is the air adhering to the posterior mixture alone, amounting only to 6 grms., which enters the eudiometer and affects the accuracy of the analysis.

2nd. From the principle of the method, the accuracy of the results depends upon the correctness of the *carbon* determination.

3rd. It is impossible to introduce the potash-ball into the eudiometer without at the same time admitting a little air.

If greater accuracy be sought than can be attained by this method, or if a body poor in nitrogen is to be analyzed, the following or absolute method must be employed, in which almost all these sources of error are avoided.

ABSOLUTE METHOD.

The principle of this method is the same as that of Dumas. A known weight of the substance intended for analysis is burnt in a tube from which the atmospheric air has been previously expelled by means of carbonic acid, and the gaseous products are collected over mercury in a gas-vessel containing a solution of caustic potash. All the carbonic acid is absorbed, and nothing but nitrogen is left. The volume of the latter is afterwards ascertained, and its weight determined by calculation.

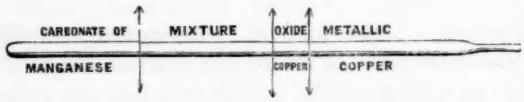
To furnish the carbonic acid required in this process, I have always employed carbonate of manganese in preference to bicarbonate of soda or carbonate of copper, which are usually employed in processes of this description, as it contains more available carbonic acid, and I believe less water than those substances. It may be economically prepared from the impure chloride of manganese, which accumulates to such an extent in most laboratories from the preparation of chlorine gas. This is evaporated to dryness, dissolved in water, filtered, and a solution of carbonate of soda added gradually, till all the iron is thrown down. The liquor is again filtered, and treated now with an excess of carbonate of soda, which precipitates all the manganese as carbonate. The precipitate is well washed by decantation, dried in a water-bath, and preserved in a well-stoppered bottle for use.

In this, as in the preceding method, oxide of mercury is employed as the agent of combustion, and must be prepared in the same manner. I will now give a detailed account of the process.

A combustion-tube of hard glass, 2½ to 3 feet in length and

having tolerably thick walls, is selected, and sealed at one end. Twelve grammes of carbonate of manganese are now intimately mixed in a mortar with 2 grms. of oxide of mercury, and the mixture is transferred to the tube (Fig. 4). The oxide is added in order to prevent the possible formation of carbonic oxide, from the presence of organic matter in the manganese, or from other causes. At a distance of 1 inch from the carbonate, a plug of freshly ignited asbestos is placed, so that on bringing the tube into a horizontal position, a channel may be left for the passage of gas. A quantity of the substance intended for analysis, having been previously reduced to powder and dried in a water-bath till it had ceased to lose weight, is now introduced into a small glass tube, and accurately weighed. About 5 or 6 decigrammes of it are next carefully transferred to a well-glazed mortar, and the tube is weighed a second time, the difference between the two weighings giving the exact quantity of substance employed in the analysis. Some freshly ignited oxide of copper and oxide of mercury are now intimately mixed in a mortar, in the proportion of 2 parts of the former to $2\frac{1}{2}$ of the latter. This mixture is dried in an evaporating basin, and a quantity of it is weighed out, sufficient to furnish $4\frac{1}{2}$ grms. for the combustion of each decigramme of substance taken (6 decigrammes of substance requiring therefore 27 grms. of the mixed oxides). This will afford quite enough oxygen for the complete combustion of any organic compound. It is next added to the mortar containing the substance for analysis, and most intimately mixed with it, and the whole is transferred, without loss, to the combustion-tube, about 1 grm. of unmixed oxide of mercury having been previously introduced (Fig. 4). The mortar is then rinsed with a little pure oxide of copper and a little of the mixture, which are also transferred to the tube. A plug of asbestos is now introduced and placed at a distance of about 10 or 11 inches from the former plug, so that on bringing the tube into a horizontal position, the organic mixture may not form too thick a stratum. The asbestos should be made to sweep before it every particle of the organic mixture adhering to the walls of the tube. A quantity of pure oxide of copper, sufficient to occupy about 2 or 3 inches of the tube is next added, then another asbestos plug, and finally about 12 or 15 grms. of finely-divided metallic copper, prepared in the same manner as for the preceding process. The

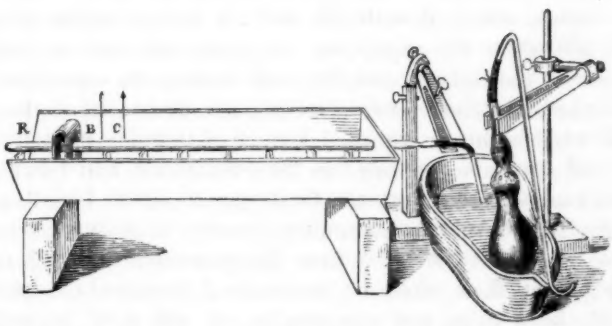
FIG. 4.



copper should be made to occupy about 7 or 8 inches of the tube (Fig. 4). The tube is now drawn out and a delivery-tube attached to it by means of a caoutchouc connector, of the same size and shape as that used in the former method, with this exception, that the extremity which is to be plunged beneath the mercury, forms a right instead of an acute angle. A few taps on a table suffice to shake together the contents of the tube, so as to leave a free passage for the evolved gases from end to end.

The tube being thus prepared, is arranged in the combustion-furnace, with 1 inch of the wide part projecting beyond it, and the delivery-tube is plunged beneath the surface of the mercury in the mercurial trough, and kept in this position by means of a wooden holder (Fig. 5). A screen is now placed over the tube, at a

FIG. 5.



distance of 1½ to 2 inches from the sealed extremity; hot coals are laid over the part so separated, *R*, for a few minutes until the carbonic acid evolved has expelled all the atmospheric air, and are then transferred to the other side of the screen and placed over the posterior half of the remaining carbonate *B*, which is heated in such a manner as to produce a pretty brisk evolution of gas. When the disengagement of gas begins to decline, the fire is extended to the anterior half of the manganese *C*, and the metallic copper and unmixed oxide in the fore-part of the tube are at the same time raised to a red heat, the organic mixture being of course protected from the heat by means of a screen. The carbonic acid in its passage over the red-hot copper and oxide, sweeps before it every trace of air mechanically adhering to them. As soon as the evolution of gas has ceased, the end of the delivery-tube, without of course allowing it to rise above the surface of the mercury, is introduced into the gas-apparatus

represented in Fig. 5, which has been previously filled carefully with mercury, with the exception of the top, which contains 16 or 17 cubic centimetres of a concentrated solution of potash, and the fire is extended to the organic mixture. During the entire combustion, that part of the tube where the exhausted manganese lies, must be maintained at a red heat.

Before proceeding further, it will be necessary to give a minute description of this gas-apparatus and the method of constructing it, particularly as I believe it will be found capable of extensive application. A glass vessel is procured, of the shape represented in Fig. 6, and having a capacity of about 200 cubic centimetres; the top should not be more than 7 or 8 millimetres in outer diameter. A tube of thick vulcanized caoutchouc, 1½ inches in length, is slipped over the top, which it must accurately fit, to the extent of half an inch, and securely bound round it with silk cord, 1 inch of tubing being thus left above the apparatus. A glass rod, half an inch long, with the ends ground flat, and having the same diameter as the caoutchouc tube, is pressed down the latter till it touches the gas-vessel. A piece of thermometer tubing, also of the same diameter as the caoutchouc and having a fine hair-bore, is now bent into the form represented in Fig. 7, and also inserted. The caoutchouc is next slightly stretched over it, and at the same time firmly secured with silk cord, so that there shall be no interval between the glass rod, bent tube, and gas-vessel. A silk cord is lastly tied round that part of the caoutchouc where the solid rod lies. Before using this apparatus, the joints must be tested by partially filling it with mercury, plunging the mouth beneath the surface of the same liquid, and observing if the level remains constant.

FIG. 6.

FIG. 7.

The joints having been thus proved perfect, the apparatus is filled with mercury and solution of potash, the delivery-tube is introduced, and the fire is extended to the organic mixture in the manner already described (Fig. 5). A slow but uninterrupted evolution of gas is kept up by gradually shifting back the screen and exposing a small quantity of the mixture at a time to the action of the fire. When the combustion has terminated, the unexhausted manganese at the sealed end of the tube is heated, and thus every trace of nitrogen is driven into the gas-apparatus. When the gas-bubbles which enter the potash are completely absorbed, the operation is at an end,

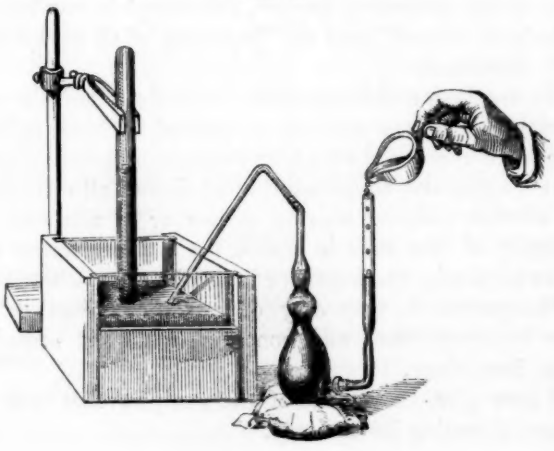
and the delivery-tube may be withdrawn from the apparatus. During the entire combustion the metallic copper in the fore-part of the tube must be kept at a full red heat.

Having thus collected all the nitrogen set free by the combustion of the organic compound, the next step is to transfer it to a eudiometer for measurement. This is done in the following manner:

A tube, of the shape represented in Fig. 8, which has been thick-
FIG. 8. ened and has had its diameter considerably reduced at *A*,

is fitted with a perforated cork, and firmly pressed into the mouth of the gas-vessel beneath the surface of the mercury Care must be taken not to introduce air at the same time with the cork. This is best avoided by moistening it with a solution of corrosive sublimate previous to introduction. Mercury is now poured into the tube till its level there is considerably higher than that in the gas-vessel. The whole apparatus is then lifted out of the mercury, carried to a mercurial trough with glass sides, and allowed to stand for one or two hours, in order that the absorption of the carbonic acid may be complete. At the expiration of this time, a eudiometer similar to that employed in the preceding process (it is of course not necessary for it to be so long), is moistened with a drop of water, carefully filled with mercury, inverted and placed beneath the surface of the mercury in the trough. The end of the bent tube attached to the gas-apparatus is now brought under the eudiometer, the centre cord is removed from the caoutchouc, and mercury poured into the upright tube (Fig. 9). By this means the gas is gradually forced

FIG. 9.



into the eudiometer. When it is nearly all transferred, the mercury must be added, drop by drop, till the potash-solution makes its appearance in the bent tube above the caoutchouc, upon which the apparatus may be removed. Great care must be taken not to allow the mercury to carry down any air-bubbles into the apparatus. This is best prevented by filling the upright tube with mercury before detaching the cord, removing all air-bubbles with a copper wire, and afterwards, when the cord is untied, by pouring in mercury according as the gas is transferred, so as to keep it nearly full. This is readily done if the caoutchouc joint has been carefully made, so as not to allow the passage of gas without considerable resistance.

We have now transferred to the eudiometer the exact quantity of gas that was in the gas-apparatus. It is true that on beginning to transfer the nitrogen, the hair-tube was full of air, which was of course driven into the eudiometer; this is, however, exactly compensated by an equal measure of nitrogen remaining behind, namely, the full of the same hair-tube, on disconnecting the apparatus. We have thus been enabled, by means of this apparatus, and by the employment of a very small quantity of mercury, not only to transfer the gas completely to the eudiometer, but also to separate it completely from the potash-solution, which, by the tension of its vapour, would afterwards interfere with the accurate measurement of the gas.

The volume of gas is now read off and properly corrected for temperature, pressure, and aqueous vapour. The actual number of cubic centimetres it occupies and its weight, are afterwards ascertained by calculation.

The advantages of this method are:

1st. As in the preceding process, the complete combustion of the organic body is secured, and the formation of all oxides of nitrogen effectually prevented.

2nd. By employing the apparatus I have described, the accuracy of a gas measurement over mercury is secured, whereas in similar processes, the nitrogen has always been hitherto measured over water.

3rd. It is applicable to the analysis of almost all nitrogenous compounds, whether rich or poor in carbon or in nitrogen, and quite independently of the state in which the latter element may exist, whether as ammonia, amidogen, or in combination with oxygen.

4th. The process is very easy of execution, requires but a few hours for its completion, and contains within it remarkably few sources of inaccuracy.

I shall now give the results of the analyses that were made for the purpose of testing its accuracy.

NARCOTINE.

Quantity taken 0·5756 grm.

	Observed vol.	Temp. C.	Height of mercury above that in trough.	Barom.	Corrected vol. at 0° C. and 760mm pressure.
Vol. of nitrogen (moist) . . .	71·67	21·0	211·2mm	754·2mm	44·97 =

15·793 cub. cents. which weigh 01989 grm. = 3·45 per cent nitrogen.

	Per cent. Theory.	Liebig.	Regnault. 1.	Regnault. 2.	Hofmann.
C_{46}	64·61	64·09	64·01	64·50	64·53
H_{25}	5·85	5·50	5·96	5·97	6·21
N	3·31	2·51	3·46	3·52	3·30
O_{14}	26·23		26·57	26·01	25·96
	100·00				

MORPHIA.

Quantity taken, 0·5562 grm.

	Observed vol.	Temp. C.	Height of mercury above that in trough.	Barom.	Corrected vol. at 0° C. and 760mm pressure.
Vol. of nitrogen (moist) . .	94·1	23·2	186·7mm	744·3mm	61·32 =

21·535 cub. cents. which weigh 0·027134 = 4·88 per cent nitrogen.

	Per cent. Theory.	Liebig.	Regnault. 1.	Regnault. 2.	Will.	Dumas.
C_{34}	71·57	72·34	72·87	72·41	72·50	72·02
H_{19}	6·66	6·366	6·86	6·84	—	7·06
N	4·91	4·995	5·01	5·01	6·72	5·53
O_6	16·86	16·299	15·26	15·74	—	14·84
	100·00					

The formula $C_{35}H_{20}NO_6$ gives 4·80 per cent nitrogen.

CODEINE.

Quantity taken, 0·5517 grm.

	Observed vol.	Temp. C.	Height of mercury above that in trough.	Barom.	Corrected vol. at 0° C. and 760mm pressure.
Vol. of nitrogen (moist) . .	88·04	20·7	197·3mm	745·6mm	56·88 =

19·976 cub. cents. which weigh 0·02517 = 4·56 per cent nitrogen.

	Per cent. Theory.	Regnault. 1.	Regnault. 2.	Gerhardt.
C_{36}	72·24	74·32	73·94	73·30
H_{21}	7·02	7·19	7·23	7·19
N	4·67	4·89	4·86	4·89
O_6	16·07	13·60	13·94	14·62
	100·00			

This formula, which is Gerhardt's, has been recently confirmed by Dr. Anderson.*

NICOTINE.

In order to secure its being perfectly anhydrous, I heated it in an oil-bath to 140° C. and maintained it at this temperature for upwards of an hour, a stream of dry hydrogen gas being passed through it at the same time.

A slight modification of the process becomes necessary, in order to adapt it to the analysis of fluids. The manganese is introduced into the combustion-tube, and then an asbestos plug as usual. A second plug is now placed at a distance of about 3 inches from the first, an empty space being left between them. A glass bulb is now made with a long neck and a hair-bore, and weighed. With the exception of the neck, it is completely filled with the fluid intended for analysis, sealed, and weighed again. A little oxide of copper is next introduced into the tube, then the bulb with the point broken off, and finally more oxide, till the neck is half covered. A mixture is now made of 15 parts of oxide of copper and 10 parts of oxide of mercury. Of this a quantity is weighed out, sufficient to furnish 8 grms. for every decigramme of fluid employed in the analysis, and transferred to the tube, of which it should occupy 8 or 10 inches. Some unmixed oxide of copper is next added, sufficient to form a stratum of 3 inches in length, and the remainder of the tube is filled as before. It is now arranged on the furnace, and the manganese is heated as usual, the bulb being kept quite cold during the passage of the gas. The metallic copper and oxide are next heated, and the fire is extended to the mixture, a small quantity of which is heated, a red-hot coal being at the same time brought near the bulb. The fire is gradually extended back to the bulb, which should be heated so as to produce a slow but constant evolution of gas. The remainder of the process is conducted as before.

* Chem. Soc. Qu. J. III, 112.

When a very volatile fluid is to be analyzed, it is advisable to employ a retort to contain the manganese.

Quantity taken, 0·3312 grm.

	Observed vol.	Temp. C.	Height of mercury above that in trough.	Barom.	Corrected vol. at 0° C. and 760^{mm} pressure.
Vol. of nitrogen (moist) . .	170·51	19·7	112·0^{mm}	744·9^{mm}	128·38 =

45·087 cub. cents. which weigh 0·056809 = 17·15 per cent nitrogen.

	Per cent. Theory.	Barral.	Melsens.
C_{10}	73·17	73·33	74·3
H_8	9·76	9·42	8·8
N	17·07	17·04	17·3
	100·00		

The formula $C_{10} H_7 N$ gives 17·28 per cent nitrogen.

NITRATE OF POTASH.

In this analysis I employed a shorter combustion-tube and less manganese. 0·5033 grm. of the nitrate, which had been previously rendered anhydrous, was weighed out, and, in order to secure complete decomposition, mixed in a mortar with 1½ grms. of perfectly dry bisulphate of potash. 12 grms. of a mixture of equal parts of oxide of copper and oxide of mercury were now added, and the whole well rubbed up together. This was transferred to the tube, and the remainder of the analysis conducted as before.

	Observed vol.	Temp. C.	Height of mercury above that in trough.	Barom.	Corrected vol. at 0° C. and 760^{mm} pressure.
Vol. of nitrogen (moist) . .	200·17	22·3	84·6^{mm}	743·2^{mm}	154·89 =

54·397 cub. cents. which weigh 0·0685402 grm. = 13·62 per cent
Theory = 13·83 „

CHLORIDE OF AMMONIUM.

In this analysis also a shorter tube and less manganese were employed.

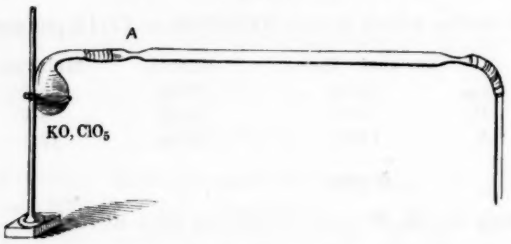
Quantity taken, 0·3101 grm.

	Observed vol.	Temp. C.	Height of mercury above that in trough.	Barom.	Corrected vol. at 0° C. and 760^{mm} pressure.
Vol. of nitrogen (moist) . .	228·37	22·7	56·5^{mm}	744·8^{mm}	184·51 =

64·799 cub. cents. which weigh 0·8164 grm. = 26·32 per cent
Theory = 26·21 „

These analyses leave little more to be desired. I believe, however, that by a very slight modification of the process, results almost absolutely accurate might be obtained. Instead of being sealed at one end, the combustion-tube is drawn out, and made so fine at *A* (Fig. 10) as to be readily fused with a mouth blowpipe.

FIG. 10.



This end is connected, by means of a cautchouc joint, with a small retort containing chlorate of potash, and the tube is filled exactly as before. It is now drawn out in front also, and a narrow delivery-tube, 30 inches in length, attached to it. It is then placed on a furnace, the end of the delivery-tube plunged beneath the surface of mercury, and the chlorate heated, by means of a lamp, for a quarter of an hour. At the expiration of this time, the lamp is removed, a small quantity of the metallic copper in the fore-part of the tube is heated, and the heat continued till the height of the mercury in the delivery-tube nearly corresponds with that of the barometer. A high temperature is by no means necessary to enable copper to absorb the oxygen, and it should be avoided. As soon as the mercury has ceased to rise in the delivery-tube, the coals are removed from the copper, and when it is nearly cold, the chlorate is once more heated for a quarter of an hour, and afterwards a fresh quantity of the metallic copper as before. When the mercury has risen a second time to the height of the barometer, the combustion-tube is sealed at *A*, and the retort is removed. The manganese is now heated, and the rest of the analysis conducted exactly as before, with this exception, that the potash solution must be saturated with nitrogen or air previous to its introduction into the gas-apparatus.

This modification I have not had time to test by experiment; but hope shortly to be able to do so. I believe it might be also applied with good effect to ths Comparative Method.

This investigation was conducted in the laboratory of Professor Bunsen, in Heidelberg. Before concluding, I cannot deny myself the pleasure of expressing my gratitude to him for his great personal kindness and valuable advice during the progress of the research.

XXIII.—*On Ethers intermediate between the Œnanthylic and the Methylic, Ethylic, and Amylic Series, and on the constitution of Castor-oil Alcohol.*

By A. W. Wills,

of University College, London.

Dr. Williamson* has shown that alcohols may be regarded as water $\begin{matrix}H\\H\end{matrix}O$, in which 1 atom of hydrogen is replaced by an organic radical, methyl, ethyl, &c., and ethers as water in which both atoms of hydrogen are thus replaced; *e. g.*, vinic alcohol $=\begin{matrix}C_2H_5\\H\end{matrix}O$;† vinic ether $=\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$. Moreover, he has shown that by acting on potassium-alcohol $\begin{matrix}C_2H_5\\K\end{matrix}O$ by the iodides of methyl, amyl, &c., intermediate ethers may be formed, containing different radicals; thus, with potassium-alcohol and iodide of methyl:

$$\begin{matrix}C_2H_5\\K\end{matrix}O + CH_3I = KI + \begin{matrix}C_2H_5\\CH_3\end{matrix}O.$$

The object of the following experiments is to show that similar intermediate ethers may be formed, containing the radical *Œnanthyl*, C_7H_{15}, together with methyl, ethyl, &c.

CASTOR-OIL ALCOHOL.

Previously to forming these ethers, some time was occupied in experiments upon the constitution of castor-oil alcohol, this substance possessing considerable interest, from its important position in the series to which it belongs, viz., probably between the caproic and caprylic alcohols. It was discovered by M. Bouis, who believed it to be caprylic alcohol $C_8H_{18}O$, and explained its formation, in the distillation of castor-oil with potash, by the following equation:‡

* Phil. Mag. [3] XXXVII, 60; Chem. Soc. Qu. J. IV, 106.

† The atomic weights used in this paper are those of Gerhardt, viz. H=1; O=16; S=32; C=12; Cl=35·5; I=126; K=39; Na=23, &c. (*Vid.* Gmelin's Handbook, Translation, VII, 17.)

‡ Compt. rend. XXXIII, 141; Chem. Soc. Qu. J. IV, 362.

$$\underbrace{C_{18}H_{34}O_3}_{\text{Ricinoleic acid.}} + 2\left(\underset{H}{}O\right) = \underbrace{C_{10}\underset{K_2}{H_{16}O_4}}_{\text{Sebate of potash.}} + \underbrace{C_8H_{18}O}_{\text{Caprylic alcohol.}} + 2H.$$

It was subsequently announced that M. Bouis had, upon further investigation, come to the conclusion that the substance in question was not caprylic but œnanthylic alcohol, $C_7H_{16}O$.*

The alcohol used in my experiments was prepared by saponifying pure castor-oil by solution of potash; separating the soap by addition of common salt; fusing the hard mass with about $\frac{1}{3}$ of its weight of solid hydrate of potash till a distinct smell of the alcohol was perceptible, in order to expel water; and, finally, distilling the mixture in charges of 5 or 6 lbs. in a copper retort.

At each distillation, about $\frac{1}{2}$ pint of turbid watery liquid came off, smelling of the alcohol, and then 9 or 10 oz. of the crude alcohol itself; care being taken to avoid the formation of empyreumatic products from decomposition of the sebate of potash at the end of the operation.

The crude oily product was then redistilled fractionally, and the parts having different boiling-points separated by a thermometer.

At the end of the operation, there remained in the retort a small quantity of yellow oily liquid, not volatile without decomposition, becoming solid on cooling, and perfectly neutral to test-paper.

The larger part of the alcohol was thus brought to the constant boiling-point of 178° C.; and in three several preparations of the substance, the same point was obtained; nor could any large portion be reduced below this point by repeated fractional distillation, a comparatively small quantity only coming over at points between 172° and 178° and above the latter degree.

Thus formed, castor-oil alcohol is a colourless, oily liquid, burning with a clear bright flame, of peculiar odour; boiling at 178°; of spec. grav. 0·792 at 16°·5 C.; insoluble in water, soluble in alcohol and ether.

The mean of several combustions closely agreeing, gave per cent:

C	72·787
H	13·669
O	13·544

Theory requires for the formula of œnanthylic alcohol, per cent:

* Instit. 1853, 257.

C	72·41	giving errors of	+0·37
H	13·79	„ „	−0·12
O	13·80	„ „	−0·24

while the numbers required for the formula of caprylic alcohol are per cent:

C	73·84
H	13·84
O	12·32

The above results appeared, therefore, to confirm the fact that the castor-oil alcohol so obtained was œnanthylic, not caprylic alcohol.

Its calculated boiling-point, taking the difference for each variation in composition by CH_2 as 19°·5 C. would be 175°·9, while that of caprylic alcohol would be 195°·4, the boiling-point of vinic alcohol being 78°·4.

As analyses and vapour-densities had been obtained by Mr. Railton, from alcohol prepared in an exactly similar manner to that which I have described and from the same samples of castor-oil, closely agreeing with the results required by theory for œnanthylic alcohol,* I did not pursue the subject further, but proceeded to form the ethers which I shall describe.

The fact that they were obtained, is in itself sufficient proof that the substance employed in their formation was the 14-carbon alcohol.

Since these experiments were made, Moschnin has obtained different results, tending to prove that the castor-oil alcohol is in reality caprylic, this view being supported by combustions and atomic weights of the baryta-salt of the conjugate sulphuric acid.†

I regret that I have not as yet had the opportunity of seeking all the confirmation I could desire of the above results. Combustions have been made, however, of several portions of liquid, prepared as above, and of various boiling-points.

A part having the fixed boiling-point 173° to 174° C., gave the following percentage:

C	71·83
H	12·37
O	15·83

* Chem. Soc. Qu. J. VI, 205.

† Ann. Ch. Pharm. LXXXVII, 111; Chem. Gaz. Nov. 15, 1853.

Theory requires for $C_7 H_{16} O$:

	Errors
72·41	−0·58
13·79	−1·42
13·80	+2·04

A portion boiling at 175° to 175°·5 gave:

C	72·16	showing errors of	−0·25
H	13·42	„ „	−0·37
O	14·42	„ „	+0·63

From these figures it might be expected that the boiling-point of the pure substance would lie between 175° and 178°, while it is somewhat remarkable that a very small portion was obtained between these points.

Most of the analyses were performed immediately after the distillation of the liquids, but no such change occurred by standing as that mentioned by Moschnin. All the combustions were made with oxide of copper and a stream of oxygen gas.

An attempt was made to form the pure baryta-salt of the corresponding acid, by acting upon the alcohol with equivalent quantities of bichromate of potash and sulphuric acid, distilling off nearly to dryness, neutralizing by hydrate of baryta, again distilling to remove alcohol, and crystallizing after removal of excess of baryta by carbonic acid and subsequent boiling. The pearly crystalline scales obtained after slight evaporation were removed, pressed between folds of blotting-paper and dried *in vacuo*. By further evaporation, a second crystallization was obtained, and in a similar manner four crops were produced.

The determination of the atomic weights of the first two and the last, proved that the acidified portions had taken up too much oxygen and had been partially converted into acids lower in the series than the one sought; as indeed would appear to be necessarily the case, from the fact of a considerable portion of alcohol remaining unoxidized, although all the chromate of potash appeared to have been reduced.

The percentages of baryta were:

1st salt.	2nd ditto.	4th ditto.
39·57	41·03	42·95

Œnanthylate of baryta contains per cent 38·76; caproate of baryta, the next term in the series, 41·71. It seems doubtful how far this

method of oxidation is adapted to the production of pure acids, although capable of effecting the acidification of large quantities of alcohols very readily.

Vapour-densities of the alcohol were also determined, but were uniformly found considerably higher than is required by theory, the mean of several experiments being 4·57.

This result would lead to the same conclusion as that of the combustions (in which there was a slight excess of carbon and deficiency of hydrogen), viz. : that the alcohol was contaminated with some substance more highly oxidized, probably formed by the decomposition of the sebate of potash ; and this supposition is confirmed by the fact, that in forming one of the ethers, a body was eliminated, of higher and more uncertain boiling-point, and containing also a higher percentage of carbon ; in fact, of such a constitution as might arise from the treatment of such a body as the one alluded to.

An attempt was also made to form iodide of œnanthyl, by the alternate action of iodine and phosphorus upon the alcohol, until solid iodide of phosphorus was deposited. The dark liquid produced was heavier than water, and when washed and distilled from lime and mercury, began to boil at 126° C., from which it rose quickly to 191° or 192°, at which point the greater part came over. The distillate was colourless while hot, but became dark upon cooling. Redistilled from chloride of calcium, it came over as before, mostly at 191° to 192°.

Another portion, similarly prepared, was washed with dilute carbonate of soda, then boiled with solution of potash to decompose hydriodic acid, &c., and distilled off chloride of calcium. The distillate was decolourized by a very small fragment of phosphorus, again washed with potash and placed over sulphuric acid to dry. It had a somewhat higher boiling-point than the former portions, viz. about 196°.

Taking the boiling-point of iodide of ethyl as 73° C., and that of iodide of amyl as 146°, the calculated point of iodide of œnanthyl would be 194°·5.

Although no difference has hitherto been recognized between samples of castor-oil from different sources, it seems probable either that such a difference really exists, and hence that the products obtained by its treatment may by characterized by a corresponding variation, or that, according to the manner of operation, especially in regard to the quantity of alkali used in saponification and distillation, sometimes one alcohol, sometimes the other, or possibly a mixture of the two may be obtained, together with occasional products of a different

constitution. And it may here be observed, that both Bouis and Moschnin employed a process somewhat different from that described in this paper, inasmuch as they heated the oil directly with potash, without previous saponification.

It is difficult to avoid this conclusion when we observe that M. Bouis himself arrived, in a first examination, at the formula for the higher, and in a second at that for the lower alcohol, and when a like discrepancy is seen in the results of other experimenters.

Nine-carbon ether; Ethyl-œnanthyl ether, $\begin{matrix} C_2H_5 \\ C_7H_{15} \end{matrix}$ O.

It was first attempted to form this ether by acting on sodium-œnanthyl alcohol $\begin{matrix} C_7\,H_{15} \\ Na \end{matrix}$ O, by iodide of ethyl, as long as any action ensued, and removing the last traces of alcohol by sodium; but it was found that the decompositions which occurred were indefinite; the continued action of sodium being, in fact, shown by analysis to deoxidize the alcohol or ether, and to give rise to substances containing a smaller percentage of oxygen than either of the former, as is evident from the following figures.

	A.			B.	C.	
	1.	2.	Mean.			Theory requires for $C_9H_{20}O$.
C	74·44	74·37	74·40	76·81	76·65	75·00
H	13·66	13·34	13·50	14·70	16·42	13·88
O	11·89	12·28	12·09	8·48	6·92	12·11

A. being figures obtained by analysis of a portion of liquid obtained as above, of boiling-point 175° to 176° C.

B. by that of the same liquid after long action of potassium upon it.

C. by the combustion of a similar portion after more prolonged action.

It was thought possible, that by very long action, the hydrocarbon C_7H_{14}, or the intermediate hydrocarbon C_9H_{18}, might be produced; but after some hours, the action became sluggish, and would probably have ceased entirely before the desired effect was nearly produced.

The action by indefinite quantities of the several materials, failing therefore to produce the required body in a state of exact purity, the experiment was repeated with *equivalent* quantities of œnanthylic

alcohol, sodium, and iodide of ethyl. The latter was prepared in the ordinary way, by the action of phosphorus and iodine on absolute alcohol, and had a boiling-point of 73° C. Half the alcohol was first acted upon by half the sodium, and then half the iodide added and slight heat applied. Much iodide of sodium was deposited, and the smell of the iodide ceased. More sodium and iodide were then added, in small portions at a time, the former acting with difficulty, but the action being renewed upon removal of the sodium and addition of a little more iodide. When the latter was accidentally added in excess, small quantities of fresh material were taken, also in equivalent weights, and the sodium-alcohol they supplied was added in excess to the mixture previously containing excess of iodide of ethyl.

The action being completed, the liquid was distilled off from the residue of iodide of sodium, without using potassium to remove traces of alcohol, and introduced into a small retort, from which it was distilled fractionally with a thermometer.

It began to boil at 137° or 138° C., and rose quickly to 177°, at which point the larger part came over, a small portion only passing above this point.

The liquid so obtained was colourless and mobile, having the peculiar generic smell of all œnanthyl compounds, although distinct from that of the alcohol; it burns with a clear luminous flame, is insoluble in water, soluble in ether and alcohol; boils at 177° C., and its spec. grav. is 0·791 at 16°.

The close correspondence of this body with the alcohol in boiling-point and specific gravity, suggested the possibility of the following transformation having taken place, although there were no signs of its occurring, such as evolution of olefiant gas:

$$C_7 \begin{matrix} H_{15} \\ Na \end{matrix} O + C_2 H_5 I = Na I + C_7 H_{16} O + C_2 H_4,$$

the ether $C_9 H_{20} O$ being in fact resolved into the alcohol and olefiant gas; but combustions proved it to be really the ether.

0·2279 grm. of liquid gave $HO = 0·2968$ and $CO_2 = 0·6281$, corresponding to:

	Per cent.	Theory requires for formula $C_9 H_{20} O$.
C	75·16	75·00
H	14·44	13·88
O	10·38	11·11

In taking the specific gravity of the vapour of this substance, and in all similar experiments, the globes were filled with dry hydrogen previously to introduction into the oil-bath, in the manner described by Mr. Railton,* in order to prevent the blackening and oxidation of the substance, which otherwise takes place at the high temperature necessarily employed in the experiment.

The following results were obtained:

Weight of globe full of dry air at 21° C. and bar. 29·72 in.	76·5009 grms.
Globe sealed at 242° C. and bar. 29·73 in.	
Globe with condensed vapour at 20° C. and bar. 29·73 in.	77·2740 „
Capacity of globe	22·1 cub. in.
Residual hydrogen at 21° C. and bar 29·73 in.	0·2 „

These figures give as the spec. grav. 5·095; calculation gives 4·998; error, ·097.

EIGHT-CARBON ETHER; METHYL-ŒNANTHYL ETHER, $\begin{matrix} C\ H_3 \\ C_7\ H_{15} \end{matrix}$ O.

This ether was prepared in a manner strictly analogous to that employed in forming the 9-carbon ether. The iodide of methyl used had the boiling-point 43° C.

After each addition of iodide, the liquid was distilled off in an oil-bath from the iodide of sodium deposited, and then the whole fractionally distilled.

A small portion came off below 154° C., smelling of iodide of methyl; the boiling-point then rose steadily to 161°·5, between which point and 162°·5, most came over; thence to 164°—166°.

The part boiling at 161°·5 to 162°·5 was redistilled over a spirit-lamp, and came over almost entirely at 161°—162°; a little at 162°—163°.

The small portion coming over first at 162° to 164° also yielded a portion at 161°—162°, most remaining at the same points as before.

The entire portion boiling at 161°—162° was now distilled upwards with a small fragment of sodium, in order to destroy the last traces of alcohol. A slight action ensued upon the application of a gentle heat; and when this had ceased, the liquid was distilled off at 160°·5—161°, except a few drops only above that point.

* Chem. Soc. Qu. J. VI, 205.

It is a colourless, mobile body, of strong smell, insoluble in water, soluble in alcohol and ether; of boiling-point 160°·5—161°, and of spec. grav. 0·830 at 16°·5.

For some reason, I found unusual difficulty in burning this body, even with a stream of oxygen, a difficulty the cause of which is not apparent from the constitution of the substance.

The following were the results of analyses:

I.	0·1890	grm.	ether	gave	CO_2	0·5078	and HO 0·2423
II.	0·1534	„	„	„	„	0·4118	„ 0·1924
III.	0·1098	„	„	„	„	0·2949	„ 0·1427

Corresponding to per cent:

	I.	II.	III.	Mean [omitting (H, III)].
C	73·280	73·213	73·251	73·248
H	14·243	13·930	(14·422)	14·086
O	12·477	12·857	12·327	12·666

It appears from these figures, that the substance obtained was the ether sought, but not in a state of complete purity, for theory requires for the formula $C_8 H_{18} O$, per cent:

C	73·846
H	13·846
O	12·308

A portion of the liquid obtained in the above process, of boiling-point 162°—164°, was also analyzed and gave per cent:

C	74·72
H	13·68
O	11·48

It was to this substance that allusion was made, as perhaps affording some clue to the nature of the impurities contaminating the alcohol.

It appears, therefore, that the portion obtained with the constant boiling-point of 160°·5—161° C. is the one most nearly approaching to purity; and the fact is confirmed by the vapour-densities obtained, which are all somewhat below that required by theory.

The following were the results, the globes being sealed respectively at 217°·5 and 223° C.

Boiling-point of liquid, 160°·5—161° C.

I.	II.	Mean.
4·23	4·18	4·20

Theory requires 4·48, and the error occurs on the same side as that in the combustions, viz., as resulting from a lower percentage of carbon than that corresponding to the theoretical composition.*

There is no doubt, however, that the substance is the intermediate ether $\begin{matrix} C & H_3 \\ C_7 & H_{15} \end{matrix}$ O, in a state approaching purity.

TWELVE-CARBON ETHER; AMYL-ŒNANTHYL ETHER, $\begin{matrix} C_5 & H_{11} \\ C_7 & H_{15} \end{matrix}$ O.

In forming this ether, equivalent quantities of œnanthylic alcohol, iodide of amyl, of boiling-point 146° C., and of sodium, were taken, and a process employed analogous to that used in forming the 8- and 9-carbon ethers.

Much iodide of sodium was deposited, but the liquid, when redistilled, gave no large portion with a fixed boiling-point; it seemed most constant about 210° C. The process was therefore repeated on a larger scale; and the liquid obtained, when fractionally distilled, began to boil at 152°, and rose gradually to 177°, between which point and 180°, a good deal, apparently of undecomposed alcohol, came over. Thence the boiling-point rose to 219° or 220°, and remained stationary for some time at 220° to 221°; the last portions then rapidly rose to 230° and above.

The portion boiling at 220° to 221° C., was a colourless, mobile liquid, of strong odour and burning taste, soluble in ether and alcohol, but not in water; burning with a clear bright flame, volatile without decomposition, and of spec. grav. 0·608 at 20° C.

The calculated boiling-point of this ether (taking that of $C_8 H_{18} O$ as 161°, and that of $C_9 H_{20} O$ as 177°) would be 225°.

Combustions gave per cent:

C	76·99
H	13·78
O	9·23

* Two experiments gave as the density of the vapour of the portion boiling at the higher point, the numbers 4·70 and 4·77, the globes being sealed at 234° and 214° C. respectively.

	Theory requires.	Error.
C	77·42	−0·42
H	13·97	−0·19
O	8·61	+0·62

This result is confirmed by the vapour-density, which was found to be 6·57, while calculation gives 6·47.

An attempt was also made to form this ether by the mutual action of equivalent quantities of amylic and œnanthylic alcohols, together with enough sulphuric acid to convert the latter into sulphœnanthylic acid; but it was not attended with success, the application of a very moderate heat producing blackening and decomposition, and no etherification occurring at the temperature which it was possible to apply without producing this effect.

In conclusion, I take this opportunity of expressing my obligation to Dr. Williamson for his advice and assistance during the progress of these experiments.

PROCEEDINGS

AT THE

MEETINGS OF THE CHEMICAL SOCIETY.

November 7, 1853.

WARREN DELARUE, Esq., in the Chair.

The following donations were announced:

"The Quarterly Journal of the Geological Society:" from the Geological Society.

"The Literary Gazette" for July, August, September, and October: from the Publishers.

"Bulletin de la Société Vaudoise des Sciences Naturelles," No. 1.

The following communications were read:

"On the Constitution of Salts considered as Substitution-products formed on the Type of Water," by Dr. Odling.

"On New Methods for the determination of Nitrogen in organic and inorganic Compounds," by Dr. Maxwell Simpson.

November 21, 1853.

ROBERT PORRETT, Esq., Treasurer, in the Chair.

The following donations were announced:

"The Transactions and Proceedings of the Royal Society of Edinburgh, for the session 1852-3:" from the Society.

"The Literary Gazette."

"The Journal of the Society of Arts."
"The Journal of the Photographic Society."
"The Medical Circular."
"Taylor's Calendar of Scientific Meetings:" from the Publishers.
"Hand-book of Chemistry," by Messrs. Abel and Bloxam: from the Authors.

G. Downing Living, Esq., of St. John's College, Cambridge, was duly elected a Fellow of the Society.

A Paper was read:

"On Ethers intermediate between the Œnanthylic and the Ethylic, Methylic, and Amylic series:" by A. W. Wills.

December 5, 1853.

COLONEL PHILIP YORKE, President, in the Chair.

The following donations were announced:

"Bulletin de la Classe Physico-mathématique de l'Académie Impériale des Sciences de St. Pétersbourg."
"The Pharmaceutical Journal, for December:" from the Editor.
"The Literary Gazette," 2 numbers.
"The Medical Circular," 2 numbers: from the Publishers.

The following Papers were read:

"Analysis of the Ash of Lemon-juice," by Henry M. Witt.
"On the Platino-tersulphocyanides and the Platino-bisulphocyanides, two new series of salts, and their decompositions:" by George Bowdler Buckton, F.L.S.

December 19, 1853.

COLONEL PHILIP YORKE, President, in the Chair.

The following donations were announced:

"The Literary Gazette:" from the Publishers.
"The Journal of the Society of Arts:" from the Society.
"The American Journal of Science and Arts," by Professors Silliman and Dana: from the Editors.

"List of Members of the Royal Institution of Great Britain."

"Notices of Meetings of the Royal Institution:" from the Royal Institution.

"Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften," Vienna. Band x, Heft 4 & 5.

"Denkschriften der Kaiserlichen Akademie der Wissenschaften." Fünfter Band. Zweite Lieferung.

Ditto. Vierter Band. Erste Lieferung.

Tafeln zur Abhandlung.

"Beiträge zur Naturgeschichte von Chili," von Freiherrn v. Bibra.

"Proceedings of the Royal Society," from the Society.

Bronze Medal of Berzelius: from Dr. N. P. Hamberg, of Stockholm.

The following Papers were read:

"Note on Platinum accompanying Silver in solution in Nitric Acid," by Henry How.

"Note on the Valuation of Protochloride of Tin," by Dr. Penny.

"On the so-called Iodide and Chloride of Nitrogen," by J. H. Gladstone, Ph.D., F.R.S.

TITLES OF CHEMICAL PAPERS

IN

BRITISH AND FOREIGN JOURNALS,

PUBLISHED IN THE YEAR 1853.

A.

Acetates.—On the acetates and other compounds of alumina: by *Walter Crum.* Chem. Soc. Qu. J. vi, 217.

Acetimetry.—On acetimetry: by *C. G. Williams.* J. Pharm. [3] xxiv, 288.

Acetone.—Chemical examination of acetone: by *G. Städeler.* Nachr. von der Gesellsch. d. Wiss. zu Göttingen, 1853, No. 9, p. 121; Chem. Gaz. 1853, 341.

—— On the presence of methylamine in the products accompanying acetone: by *C. G. Williams.* Chem. Gaz. 1853, 409.

Acid, Acetic.—New process for manufacturing pure acetic acid: by *Christl* and *Völckel.* Chem. Gaz. 1853, 96.

.. .. New method of manufacturing pure acetic acid. Pharm. J. Trans. xiii, 176.

Anthranilic.—On anthranilic, benzamic, and carbanilidic acids: by *B. W. Gerland.* Ann. Ch. Pharm. lxxxvi, 143.

Arsenious.—On arsenious acid, its salts, and the arsenio-sulphides: by *O. B. Kühn.* Arch. Pharm. cxix, 267, and cxxi, 1; Chem. Gaz. 1853, 364.

.. .. On compact transparent sulphur and vitreous arsenious acid: by *C. Brame.* Ann. Ch. Phys. [3] xxxvii, 217.

.. .. On vitreous arsenious acid: by *C. Brame.* Comp. rend. xxxvii, 90.

Boracic.—On the influence of water on boracic acid in borates: by *H. Rose.* Chem. Gaz. 1853, 65.

.. .. On the compounds of boracic acid and water with protoxide of cobalt, protoxide of nickel, and oxide of zinc: by *H. Rose.* Pogg. Ann. lxxxviii, 299.

.. .. On the compounds of boracic acid and water with sesquioxide of iron: by *H. Rose.* Pogg. Ann. lxxxix, 473.

.. .. On the compounds of boracic acid and water with oxide of copper: by *H. Rose.* Pogg. Ann. lxxxvii, 598.

.. .. On the compounds of boracic acid and water with oxide of lead: by *H. Rose.* Pogg. Ann. lxxxvii, 470.

.. .. On the compounds of boracic acid and water with oxide of silver: by *H. Rose.* Pogg. Ann. lxxxviii, 482.

.. .. Action of boracic acid on tincture of litmus: by *Malaguti.* Ann. Ch. Phys. [3] xxxvii, 206.

Acid, Boracic.—Note on the existence of boracic acid in several mineral waters and in various natural substances: by *E. Filhol.* Compt. rend. xxxvi, 327; Chem. Gaz. 1853, 113.

.. .. On the presence of boracic acid in the mother-liquor of the salt-springs of Bex: by *M. Baup.* J. Pharm. [3], xxiii, 43.

.. .. On the presence of boracic acid in the alkaline, sulphureous, thermal waters of Olette (Pyrénées Orientales): by *J. Bouis.* Compt. rend. xxxvi, 229.

.. .. On the presence of boracic acid in the mineral waters of Wiesbaden and Aix-la-Chapelle: by *Fresenius* and *Wildenstein.* J. pr. Chem. lv, 163; J. Pharm. [3] xxiii, 76.

Camphomethylic.—On camphomethylic acid: by *A. Loir.* Ann Ch. Phys. [3] xxxvii, 196: xxxviii, 483.

Camphoric.—On lævo-camphoric acid and lævocamphor: by *J. Chautard.* Compt. rend. xxxvii, 166.

Caproic.—Note on the preparation of propionic and caproic acids: by *A. W. Williamson.* Phil. Mag. [4] vi, 204.

Caprylic.—On anhydrous caprylic acid: by *L. Chiozza.* Compt. rend. xxxv, 865; Ann. Ch. Pharm. lxxxv, 229; Chem. Gaz. 1853, 88.

Carbonic.—Action of carbonic acid on tincture of litmus: by *J. Malaguti.* Ann. Ch. Phys. [3] xxxvii, 206.

.. .. Apparatus for the determination of carbonic acid: by *Max. Scheffner.* Chem. Gaz. 1853, 37.

.. .. Action of carbonic acid on quinine and cinchonine; formation of crystallized carbonate of quinine: by *M. Langlois.* Compt. rend. xxxvii, 727.

.. .. Note on an apparatus for estimating carbonic acid: by *M. de Luca.* Compt. rend. xxxvii, 730.

Citric.—Researches on the fermentation of citric acid: by *J. Personne.* Compt. rend. xxxvi, 197; Chem. Gaz. 1853, 147.

.. .. Improvements in the manufacture of citric and tartaric acid (Price's Patent). Pharm. J. Trans. xiii, 46.

Formic.—On the presence of formic acid in the human secretions: by *D. Campbell.* Chem. Gaz. 1853, 310.

Fumaric.—On the occurrence of fumaric acid in *Corydalis bulbosa:* by *W. Wicke.* Ann. Ch. Pharm. lxxxvii, 225.

Gallic.—On the preparation of gallic acid from Chinese gall-nuts: by *G. C. Wittstein.* Pharm. J. Trans. xii, 444.

Hippuric.—Reproduction of hippuric acid: by *M. Dessaignes.* Compt. rend. xxxvii, 251; Ann. Ch. Pharm. lxxxvii, 325.

Hydrochloric.—Volumetrical determination of sulphuric and hydrochloric acid: by *M. Levol.* Chem. Gaz. 1853, 378.

Hydrocyanic.—Determination of the strength of hydrocyanic acid: by *J. Robertson.* Pharm. J. Trans. xiii, 105.

.. .. On the estimation of iron, cyanogen, hydrocyanic acid, and hydrosulphocyanic acid by volume analysis; and on the quantitative determination of the sulphocyanide of potassium in saliva: by *T. J. Herapath.* Chem. Gaz. 1853, 294.

Hydroferrocyanic.—Preparation of hydroferrocyanic acid. Ann. Ch. Pharm. lxxxvii, 127.

Acid, Hydrofluoric.—On the preservation of hydrofluoric acid: by *G. Städeler*. Ann. Ch. Pharm. lxxxvii, 137.

Hydrosulphuric.—On the action of sulphuretted hydrogen on picric acid: by *A. Girard*. Compt. rend. xxxvi, 421.

Kyanurenic.—On kyanurenic acid: by *J. Liebig*. Chem. Soc. Qu. J. vi, 112; Ann. Ch. Pharm. lxxxvi, 125; Ann. Ch. Phys. [3] xxxviii, 488.

Meconic.—On meconic acid and its derivatives: by *H. How*. Ed. Phil. Trans. xx, pt. 3, 401; *abstr.* Chem. Soc. Qu. J. vi, 72.

Moritannic.—On the formula of moritannic acid: by *R. Wagner*. Chem. Gaz. 1853, 175.

Nitric.—On the preparation of chemically pure nitric acid, and of the nitrates of potash and soda: by *C. Weber*. Pharm. J. Trans. xii, 596.

.. .. On the manufacture of nitric acid. Pharm. J. Trans. xii, 428.

.. .. On nitric acid as a source of the nitrogen found in plants: by *G. Wilson*. Trans. Roy. Soc. Edinb. xx, 591.

.. . Were the ancient Egyptians acquainted with nitric acid? by *T. J. Herapath*. Phil. Mag. [4] v, 339.

.. .. On the supposed conversion of ammonia into nitric acid in the animal organism: by *C. Jaffé*. Pharm. J. Trans. xiii, 232.

.. .. New test for nitric acid and the nitrates: by *E. W. Davy*. Phil. Mag. [4] v, 330; J. Pharm. [3] xxiv, 206.

Oleic.—Purification of oleic acid and application to manufacturing purposes (Wilson's Patent). Pharm. J. Trans. xii, 551.

Oxalic.—On the volumetric determination of oxalic acid: by *F. Liesking*. Chem. Gaz. 1853, 472.

Oxylizaric.—On oxylizaric acid (purpurin): by *H. Debus*. Ann. Ch. Pharm. lxxxvi, 117.

Paracitric.—On paracitric acid and the paracitrates: by *F. L. Winckler*. Jahrb. f. pr. Pharm. xxv, 65; Chem. Gaz. 1853, 32.

.. .. On the identity of Winckler's paracitric acid with malic acid: by *L. Pasteur*. J. Pharm. [3], xxiv, 75.

Pelargonic.—On anhydrous pelargonic acid: by *L. Chiozza*. Compt. rend. xxxv, 865; Ann. Ch. Pharm. lxxxv, 231; Chem. Gaz. 1853, 88.

.. .. On a compound of pelargonic acid with nitric oxide: by *L. Chiozza*. Ann. Ch. Pharm. lxxxv, 225; Chem. Gaz. 1853, 123.

Permanganic.—On permanganic acid. Ann. Ch. Pharm. lxxxvi, 373.

Phosphoric.—On the apparent volatilization of phosphoric acid from acid solutions, and on the action of hydrochloric acid on phosphate of soda: by *R. Fresenius*. Ann. Ch. Pharm. lxxxvi, 216.

.. .. Estimation of phosphoric acid and the phosphates by means of nitrate of uranium: by *M. Leconte*. Pharm. J. Trans. xiii, 80.

.. .. On the determination of phosphoric acid: by *E. T. Bennett*. Chem. Gaz. 1853, 17.

Picric.—Action of sulphuretted hydrogen on picric acid: by *A. Girard*. Compt. rend. xxxvi, 421.

.. .. Means of detecting picric acid in beer: by *J. L. Lassaigne*. Pharm. J. Trans. xiii, 139.

.. .. On the use of picric acid for distinguishing vegetable and animal fibres in stuffs: by *J. J. Pohl*. Sitzungsber. d. Akad. d. Wiss. zu Wien, ix, 387; Pharm. J. Trans. xiii, 183; Chem. Gaz. 1853, 320.

Acid, Propionic.—Note on the preparation of propionic and caproic acids: by *A. W. Williamson.* Phil. Mag. [4] vi, 204.

Pyrogallic.—Pyrogallic acid in wood-vinegar. Ann. Ch. Pharm. lxxxvii, 256.

Pyromeconic.—On some salts and products of decomposition of pyromeconic acid: by *J. Brown.* Phil. Mag. [4] iv, 16; *abstr.* Chem. Soc. Qu. J. vi, 78.

Pyromucic.—Preparation of pyromucic acid: by *A. E. Arppe.* Ann. Ch. Pharm. lxxxvii, 237.

Racemic.—New facts relating to the history of racemic acid: by *M. Kestner.* Compt. rend. xxxvi, 17.—Remarks on the preceding: by *M. Biot.* Ibid. 18.

.. .. Notice respecting the origin of racemic acid: by *M. Pasteur.* Compt. rend. xxxvi, 19.

.. .. On racemic acid. Pharm. J. Trans. xiii, 110.

Salicylic.—On the sensibility of the reactions of salicylous and salicylic acids on sesquioxide of iron: by *A. Dollfus.* J. Pharm. [3] xxiv, 202.

Salicylous.—On the formation of salicylous acid in the flowers of *Spiræa ulmaria:* by *L. A. Buchner.* J. Pharm. [3] xxiii, 321; Pharm. J. Trans. xiii, 87.

Sebacic.—On sebacic acid: by *M. Carlet.* Compt. rend. xxxvii, 128; J. Pharm. [3] xxiii, 176.

.. .. On an apparently new mode of formation of sebacic acid, and on the constitution of the acids $C_n H_{n-2} O_8$.: by *R. Wagner.* Chem. Gaz. 1853, 155.

Stearic.—On the solid compound obtained by distilling stearic acid with lime: by *T. H. Rowney.* Chem. Soc. Qu. J. vi, 97.

Sulphuric.—Researches on the congelation and ebullition of the hydrates of sulphuric acid: by *C. Marignac.* Ann. Ch. Phys. [3] xxxix, 184.

.. .. On the analysis of oils by means of sulphuric acid: by *M. Maumené.*

. .. On the manufacture of sulphuric acid: by *M. Gautier.* Compt. rend. xxxvii, 177.

.. .. Improvements in the manufacture of sulphuric acid (Bell's Patent). Pharm. J Trans. xii, 451.

Tannic.—On the preparation of the tannic acid: by *B. Sandrock.* Chem. Gaz. 1853, 199; Pharm. J. Trans. xii, 597.

Tartaric.—Transformation of the two tartaric acids into racemic acid. Discovery of inactive tartaric acid. New method of separating racemic acid into dextro- and lævo-tartaric acid: by *L. Pasteur.* Compt. rend. xxxvii, 162; Chem. Soc. Qu. J. vi, 77.

Uric.—Preparation of uric acid: by *A. E. Arppe.* Ann. Ch. Pharm. lxxxvii, 237.

Valerianic.—On anhydrous valerianic acid: by *L. Chiozza.* Chem. Gaz. 1853, 52.

.. .. On the cacodyl of valerianic acid: by *W. Gibbs.* Ann. Ch. Pharm. lxxxvi, 222; Chem. Gaz. 1853, 125.

Acids.—On the acids contained in fungi: by *P. Bolley.* Ann. Ch. Pharm. lxxxvi, 44; Chem. Gaz. 1853, 291.

Acids.—On the compounds of glycerine with acids: by *M. Berthelot.* Compt. rend. xxxvi, 27; Chem. Gaz. 1853, 121.

—— On the acids of rape-oil: by *G. Städeler.* Ann. Ch. Pharm. lxxxvii, 133.

—— On the acid formed when potash acts on oil of bitter almonds: by *Prof. Gregory.* Proc. Roy. Soc. of Edinb. 1852-53, 195.

—— Action exerted by acids and by alkaline and earthly chlorides on oil of turpentine, sugar, alcohol, and wood-spirit: by *M. Berthelot.* Ann. Ch. Phys. [3] xxxviii, 38.

Acids Anhydrous.—Researches on the anhydrous organic acids: by *C. Gerhardt.* Ann. Ch. Phys. [3] xxxvii, 285; Ann. Ch. Pharm. lxxxvii, 57, 129.

.. .. On anhydrous organic acids: by *L. Chiozza.* Ann. Ch. Pharm. lxxxiv, 106; lxxxv, 229; lxxxvi, 259; Compt. rend. xxxvi, 632; Ann. Ch. Phys. [3] xxxix, 196; Chem. Soc. Qu. J. vi, 184.

.. .. Additional researches on the anhydrous acids: by *C. Gerhardt* and *L. Chiozza.* Compt. rend. xxxvi, 1050; Ann. Ch. Pharm. lxxxvii, 290

.. .. Report on a memoir by M. Gerhardt, entitled: "Researches on the anhydrous organic acids": by *M. Dumas.* Compt. rend. xxxvi, 505; J. Pharm. [3], xxiv, 81; Pharm. J. Trans. xiii, 71.

.. .. On Gerhardt's discovery of anhydrous organic acids: by *A. W. Williamson.* Chem. Gaz. 1853, 137.

Fatty.—Researches on the fatty acids: by *W. Heintz.* Chem. Gaz. 1853, 41.

.. .. On the use of the fatty acids as a source of light: by *J. Cambacères.* Chem. Gaz. 1853, 175.

Isomeric.—Facts relating to the history of the isomeric acids: by *J. Gottlieb.* Ann. Ch. Pharm. lxxxiii, 227; Ann. Ch. Phys. [3] xxxviii, 363. Farther: Ann. Ch. Pharm. lxxxv, 17.

Organic.—On certain organic acids: by *L. Chiozza.* Compt. rend. xxxvi, 701.

Æsculin.—Addendum to the memoir on æsculin: by *Fr. Rochleder.* Ann. Ch. Pharm. lxxxvii, 200.

—— On æsculin: by *F. Rochleder* and *R. Schwartz.* Ann. Ch. Phys. [3] xxxviii, 373; J. Pharm. [3] xxiv, 292.

Affinity.—Researches on chemical affinity: by *R. Bunsen.* Ann. Ch. Pharm. lxxxv, 137; Ann. Ch. Phys. [3] xxxviii, 344; Chem. Soc. Qu. J. vi, 82.

—— On chemical affinity: by *H. Debus.* Ann. Ch. Pharm. lxxxv, 103; lxxxvi, 156; lxxxvii, 238.

Air.—Researches on the composition of atmospheric air: by *V. Regnault.* Ann. Ch. Phys. xxxvi, 385.

—— On the composition of the air contained in vegetable mould: by *Boussingault* and *Lévy.* Ann. Ch. Phys. [3] xxxvii, 5.

—— Specific heat of air: by *W. J. M. Rankine.* Phil. Mag. [4] v, 437.

Air-pump.—Improvements in the air-pump: by *M. Bretton.* Compt. rend. xxxvi, 587.—Report thereupon: by *M. Regnier.* Ibid. 1068.

Albumin.—On albumin and casein: by *N. Lieberkühn.* Pogg. Ann. lxxxvi, 117, 298; *abstr.* J. Pharm. [3] xxiii, 398.

—— On the presence of albumin in milk in the normal state: by *M. Quévenne.* J. Pharm. [3] xxiv, 94.

Albumin.—New observations on albuminoïdal substances: by *M. Panum*. Ann. Ch. Phys. [3] xxxvii, 237; J. Pharm. [3] xxiii, 238.

—— Researches on albuminoïdal substances: by *C. Leronte* and *A. de Goumuens*. Compt. rend. xxxvi, 837; J. Pharm. [3] xxiv, 17.

Alcohol.—New process for recognizing the presence of alcohol in essential oils: by *M. Oberdörfer*. J. Pharm. [3] xxiv, 73.

—— Action exerted by acids and by alkaline and earthy chlorides on alcohol: by *M. Berthelot*. Ann. Ch. Phys. [3] xxxviii, 38.

Alcohols.—On the acidification of alcohols by oxygen gas or atmospheric air: by *R. Railton*. Chem. Soc. Qu. J, vi, 205.

—— On the atomic weight and constitution of the alcohols: by *F. Wrightson*. Phil. Mag. [4] vi, 88.

—— On butylic alcohol: by *A. Wurtz*. Ann. Ch. Pharm. lxxxv, 197.

—— On caproic alcohol: by *M. Faget*. Compt. rend. xxxvii, 730.

—— On caprylic alcohol: by *Wladimir Moschnin*. Ann. Ch. Pharm. lxxxvii, 111.

—— On propionic alcohol: by *G. Chancel*. Compt. rend. xxxvii, 410; Chem. Soc. Qu. J. vi, 287.

Aldehyde.—On the occurrence of aldehyde among the products of the distillation of sugar: by *C. Völckel*. Ann. Ch. Pharm. lxxxvii, 303.

—— On aldehyde-ammonia. Ann. Ch. Pharm. lxxxvi, 375.

Aldehydes.—On a new mode of formation of the aldehydes: by *L. Chiozza*. Ann. Ch. Pharm. lxxxv, 232.

Alkali.—Improvements in the manufacture of alkali (Greenshield's Patent). Chem. Gaz. 1853, 438.

Alkalies.—New and ready method of determining the alkalies in minerals: by *J. L. Smith*. Sill. Am. J. [2] xv, 234; xvi, 53; Chem. Gaz, 1853, 252, 333.

—— Researches on the cinchona alkaloïds: by *L. Pasteur*. Compt. rend. xxxvii, 110; J. Pharm. [3] xxiii, 16; Chem. Soc. Qu. J. vi, 273.

—— On the tests for the cinchona alkaloïds: by *F. L. Winckler*. Pharm. J. Trans. xii, 422.

—— Researches on a new alkali (piperidine), derived from piperine: by *A. Cahours*. Ann. Ch. Phys. [3] xxxviii, 38.

—— Production of the ethylic and methylic alkaloïds by means of chloride of ammonium: by *M. Berthelot*. Ann. Ch. Phys. [3] xxxviii, 38.

—— On some new basic products obtained by the decomposition of the vegetable alkaloïds: by *H. How*. Chem. Soc. Qu. J. vi, 125.

—— Action of alkalis on sugar. Pharm. J. Trans. xii, 348, 393.

—— General process for the detection of the alkaloïds in cases of poisoning: by *G. Stas*. Pharm. J. Trans. xiii, 132.

Alloxan.—On a spontaneous metamorphosis of alloxan: by *Prof. Gregory*. Proc. Roy. Soc. Edinb. 1852-53, 197; Ann. Ch. Pharm. lxxxviii, 126.

Alloys—On alloys considered with reference to their chemical constitution: by *A. Levol*. Ann. Ch. Phys. [3] xxxix, 163.

—— On the position of alloys and amalgams in the thermo-electric series: by *W. Rollmann*. Pogg. Ann. lxxxix, 90.

—— On the analysis of alloys of copper and zinc: by *H. Spirgatis*. J. pr. Chem. vii, 184; Chem. Gaz. 1853, 260.

—— Note on a new alloy of silver: by *G. Barruel*. Chem. Gaz. 1853, 15.

Alloys.—Improvements in depositing alloys of metals (Marris and Johnston's Patent). Pharm. J. Trans. xiii, 233.

Alum.—Note on cubic alum: by *H. Loewel.* Compt. rend. xxxvi, 595.

Alumina.—On the presence of alumina in Bog-head coal, and on the use of the ashes of the latter in the manufacture of alum: by *T. J. Herapath.* Chem. Gaz. 1853, 169.

—— On the acetates and other compounds of alumina: by *Walter Crum.* Chem. Soc. Qu. J. vi, 217.

—— New reagent for precipitating alumina from its acid solutions: by *M. Tissier.* Compt. rend. xxxvii, 245.

—— On the separation of alumina from oxide of chromium: by *Dexter.* Pogg. Ann. lxxxix, 142.

Amalgamation.—On the reactions on which the American amalgamation process depends, and on the extraction of silver by means of amalgamation: by *Dr. Karsten.* Chem. Gaz. 1853, 141.

Amber.—On cavities in amber containing gases and liquids: by *D. Brewster,* Phil. Mag. [4] v, 233.

Amides.—Researches on the amides: by *C. Gerhardt* and *L. Chiozza.* Ann. Ch. Pharm. lxxxvii, 296; Chem. Soc. Qu. J. vi, 193.

—— Note on the theory of the amides: by *A. Wurtz.* Compt. rend. xxxvii, 246, 357.

—— Note on the theory of the amides: by *C. Gerhardt.* Compt. rend. xxxvii, 281.

Ammonia.—Note on the use of graduated solutions for determining the quantity of ammonia in waters: by *M. Bineau.* Compt. rend. xxxvi, 1039.

—— Method of getting rid of sal-ammoniac in analysis: by *J. L. Smith.* Sill. Am. J. [2] xv, 94.

—— New researches on the ammonia in the atmosphere: by *J. Pierre.* Compt. rend. xxxvi, 694.

—— On the quantity of ammonia in rain-water collected at a distance from towns: by *M. Boussingault.* Compt. rend. xxxvii, 207.

—— On the action of ammoniacal bases upon oil of mustard: by *F. Hinterberger.* Chem. Gaz. 1853, 71.

—— On the combustion of ammonia, &c., by the green oxide of chromium: by *J. E. Ashby.* Phil. Mag. [4] vi, 97.

—— On the reaction of ammonia on certain metallic arsenites: by *A. Girard.* Compt. rend. xxxvi, 793.

—— Action of ammonia on sulphamylate of lime: by *M. Berthelot.* Compt. rend. xxxvi, 1098.

—— On the supposed conversion of ammonia into nitric acid in the animal body: by *C. Jaffé.* J. pr. Chem. lix, 238; J. Pharm. [3] xxiv, 373; Pharm. J. Trans. xiii, 232.

—— On the determination of the ammonia contained in waters: by *M. Boussingault.* Compt. rend. xxxvi, 814; Chem. Gaz. 1853, 319.

—— Manufacture of ammonia and ammoniacal salts. Pharm. J. Trans. xiii, 29, 63, 112.

—— On the fabrication of sal-ammoniac: by *MM. Möhrlin* and *Stoll.* Bull. de la Soc. industr. de Mulhouse, xxiv, 375.

Ammonia.—On the estimation of ammonia in waters: by *M. Boussingault.* Ann. Ch. Phys. [3] xxxix, 257.

Amygdalin.—On the presence of amygdalin in various plants. Pharm. J. Trans. xii, 450.

Amyl.—On the preparation of carbonate of amyl: by *J. A. Bruce.* Ann. Ch. Pharm. lxxxv, 16.

—— On the action of ammonia on sulphamylate of lime: by *M. Berthelot.* Ann. Ch. Pharm. lxxxvii, 372.

Anæsthetic Agents.—Considerations on anæsthetic agents: by *M. Jobert.* Compt. rend. xxxvi, 1031.

Analysis.—New general method of chemical analysis: by *H. Sainte-Claire Deville.* Ann. Ch. Phys. [3] xxxviii, 5.

—— On a method of volumetric analysis of very general application: by *R. Bunsen.* Ann. Ch. Pharm. lxxxvi, 265.

—— A method of getting rid of sal-ammoniac in analysis: by *J. L. Smith.* Sill. Am. J. [2] xv, 94; Chem. Gaz. 1853, 115.

—— Note on the use of chlorine in analysis: by *MM. Rivot, Beudant,* and *Daguin.* Compt. rend. xxxvii, 126; J. Pharm. [3] xxiii, 169.

—— On the use of cyanide of potassium in analytical chemistry: by *H. Rose.* Pogg. Ann. xc, 193.

—— Analytical notes: by *A. B. Northcote* and *A. H. Church.* Chem. Soc. Qu. J. vi, 53.

1. Action of caustic potash on the phosphates.
2. On the behaviour of some oxides with caustic potash in the presence of oxide of chromium.

—— Contributions to analytical chemistry: by *W. Gibbs.* Ann. Ch. Pharm. lxxxvi, 52.

Separation of manganese from potash and soda; from baryta, strontia, lime, magnesia and alumina; from zinc and nickel.

—— On volumetrical analysis. Pharm. J. Trans. xiii, 284.

Aniline.—Test for aniline. Ann. Ch. Pharm. lxxxvii, 376

—— Test for aniline: by *F. Beissenhirtz.* Chem. Gaz. 1853, 434.

Ant.—Chemical investigation of the Mexican honey-ant: by *C. M. Wetherill.* Chem. Gaz. 1853, 72.

Antimony.—On the isomeric compounds of sulphur and antimony: by *H Rose.* Ber. d. Akad. d. Wiss. zu Berlin, 1853, 242; Chem. Gaz. 1853, 290.

—— On the isomeric modifications of sulphide of antimony: by *H. Rose.* Pogg. Ann. lxxxix, 122.

—— On the compounds of sulphide of antimony with antimonic oxide: by *H. Rose.* Pogg. Ann. lxxxix, 316.

—— Action of antimony upon certain classes of salts: by *J. W. Slater.* Chem. Gaz. 1853, 329.

—— On the fluorine-salts of antimony: by *F. A. Flückiger.* Chem. Gaz. 1853, 1.

—— On the sulphide of antimony: by *F. Wackenroder.* Arch. Pharm. [2] lxxi, 207; J. Pharm [3] xxiii, 156.

—— Note on the sulphantimoniate of copper and zinc: by *Prof. Ettling.* Chem. Soc. Qu. J. vi, 140.

Antimony.--On the preparation of lakes by means of chloride of antimony Schweiz. Gewerbeblatt, xi, 217; Chem. Gaz. 1853, 275.

Antiquities.—Analyses of several artificial products of high antiquity: by *M. Girardin.* J. Pharm. [3] xxiii, 165, 252, 324.

Aqua-regia —Use of aqua-regia in testing for poisons: by *Gaultier de Claubry.* J. Pharm. [3] xxiii, 27, 209.—Remarks on the same: by *Malaguti* and *Sarzeaud.* Ibid. 296.

Arbutine.—On arbutine: by *M. Kawalier.* Ann. Ch. Phys. [3] xxxviii, 375.

—— On arbutine: by *Rochleder* and *Schwartz.* J. Pharm. [3] xxiv, 293.

Arctostaphylos.—Examination of the leaves of *Arctostaphylos Ura Ursi*: by *A. Kawalier.* Chem. Gaz. 1853, 61.

Arnica.—Adulteration of arnica leaves. Pharm. J. Trans. xii, 400.

Arsenic.—On arsenious acid, its salts, and the arsenio-sulphides: by *O. B. Kühn.* Arch. Pharm. cxix, 267, and cxxi, 1; Chem. Gaz. 1853, 364.

—— On vitreous arsenious acid: by *C. Brame.* Compt. rend. xxxvii, 90.

—— Action of arsenic upon certain classes of salts: by *J. W. Draper.* Chem. Gaz. 1853, 329.

—— On the use of molybdate of ammonia as a test for arsenic in medico-legal investigations: by *H. Struve.* J. pr. Chem. lviii, 193; J. Pharm. [3] xxiv, 374; Pharm. J. Trans, xiii, 182.

—— On the toxicological relations of arsenious and arsenic acids: by *M. Schroff.* J. Pharm. [3] xxiv, 294.

—— On the reduction of arsenic and antimony by means of cyanide of potassium: by *H. Rose.* Bericht d. Akad. d. Wiss. zu Berlin, 1853, 441; Chem. Gaz. 1853, 400.

—— On the use of aqua-regia in searching for arsenic localized in the viscera: by *Malaguti* and *Sarzeaud.* J. Pharm. [3] xxiii, 27.

—— Comparative experiments on the use of hydrate of magnesia and hydrated sesquioxide of iron as antidotes for arsenic: by *K. D. Schroff,* N. Repert. Pharm. i, 447; J. Pharm. [3] xxiii, 230; Pharm. J. Trans. xiii, 38.

—— Insolubility of native realgar ($As S_2$) in carbonate of ammonia: by *C. G. Williams.* Chem. Gaz. 1853, 252.

Arsenites.—On the action of ammonia on certain metallic arsenites: by *A. Girard.* Compt. rend, xxxvi, 793.

Ashes.—Analysis of the ashes of *Erica carnea* and *Calluna vulgaris Salisb.* and of the soils on which they grow: by *C. F. Röthe.* Ann. Ch. Pharm. lxxxvii, 118.

—— Analysis of the ashes of vetch-seed from Neufchatel: by *J. Cohen.* Ann. Ch. Pharm. lxxxiv, 288.

Asphalt.—On asphalt from Canton Neuenburg: by *C. Völckel.* Ann. Ch. Pharm. lxxxvii, 139.

Aspirator.—New gasometer, serving as a pneumatic trough and as an aspirator: by *M. Tifferau.* Compt. rend. xxxvii, 51.

—— On a new aspirator: by *T. Andrews.* Pogg. Ann. lxxxviii, 603; Ann. Ch. Pharm. lxxxv, 263.

Assaying.—Abstract of the assays performed at the École des Mines: by *MM. Rivot, Beudant, Daguin,* and *Bouquet.* Ann. Min. [5] iii, 521.

Atomic Weights.—Addition to a memoir entitled: "Researches on the relations between the atomic weights and specific heat of elementary bodies": by *M. Granier*. Compt. rend. xxxvii, 130.

—— On the relations between the atomic weights of analogous elements: by *J. H. Gladstone*. Phil. Mag. [4] v, 313.

Azobenzide.—Note upon azobenzide and seminaphthalidine: by *N. Zinin*. Bull. de St. Petersb. Phys. Math. Cl. x, 348; Ann. Ch. Pharm. lxxxv, 328; Chem. Gaz. 1853, 32.

B.

Balance.—On an improved assay balance: by *G. H. Makins*. Chem. Soc. Qu. J. vi, 36.

—— On a new balance for taking the tare of vessels. J. Pharm. [3] xxiv, 354.

Balsams.—Adulteration of Peru and Tolu balsams; by *G. Ulex*. Pharm. J. Trans. xii, 549.

Bark.—On a bark called *Heetoo*, used in Abyssinia, with some remarks on the *Korarima* and on *Koussoo*: by *J. Vaughan*. Pharm. J. Trans. xii, 587.

Barmin.—On the equivalent weights of platinum and barmium: by *T. Andrews*. Ann. Ch. Pharm. lxxxv, 255.

Baryta.—Manufacture of caustic baryta from the carbonate: by *MM. Leplay* and *Dubrunfaut*. Chem. Gaz, 1853, 388.

Bases.—Contributions to the history of the volatile bases; by *A. v. Planta* and *A. Kekulé*. Ann. Ch. Pharm. lxxxvii, 1.

Bee.—Chemical examination of the food of the queen-bee: by *C. M. Wetherill*. Chem. Gaz. 1853, 91.

Beer.—Means of detecting picric acid in beer: by *J. L. Lassaigne*. Pharm. J. Trans. xiii, 139.

Bees.—Remedy for the stings of bees. Chem. Gaz. 1853, 36.

Beet.—Note on the chemical composition of the beet-root, cultivated in the alumino-siliceous soils of the Loire-Inférieure: by *M. Bobierre*. Compt. rend. xxxvi, 31; Chem. Gaz. 1853, 154.

Benzoates.—On benzoate of potash: by *W. Gregory*, Ann. Ch. Pharm. lxxxvii, 125.

Bismuth.—Researches on bismuth: by *R. Schneider*. Pogg. Ann. lxxxviii, 46; xc, 166.

—— On *magistery of bismuth*, and certain other compounds of nitric acid with oxide of bismuth. J. Pharm. [3] xxiii, 319.

Bitter Principles.—On certain bitter principles: by *Fr. Rochleder* and *R. Schwartz*. Ann. Ch. Pharm. lxxxvii, 186; J. Pharm. [3] xxiii, 474.

Blast Furnaces.—On the arrangement of the materials in the blast furnace and the application of the waste gases: by *S. H. Blackmore*. J. Fr. Inst. [3] xxv, 188, 243.

Bleaching.—On the mode of testing the strength of bleaching liquors: by *F. Lieshing*. Chem. Gaz. 1853, 139.

Blood.—On the crystallizable matter of the blood: by *M. Lehmann*. J. pr. Chem. lviii, 95; J. Pharm. [3] xxiv, 368.

Blood.—On a new method of coagulating blood in the arteries, and its application to the cure of aneurisms: by *M. Prevaz*. Compt. rend. xxxvi, 88.

—— Further observations of the crystallizable method of the blood: by *C. G. Lehmann*. Ber. d. Gesellsch. d. Wiss. zu Leipzig. Math.-Phys. Classe, 1852, 78; Chem. Gaz. 1853, 447.

Boiler.—Note on a new steam-boiler: by *M. Boutigny*. J. Pharm. [3] xxiii, 53.

Bone.—Improvements in producing ornamental surfaces in metal, ivory, or bone (Skinner's Patent). Chem. Gaz. 1853, 59.

Bones.—On the alteration of bones in the soil: by *Kindler*. Pogg. Ann. lxxxvii, 611.

Borates.—Examination of a natural product imported from America, and partly consisting of the borates of soda and lime: by *L. R. Lecanu*. J. Pharm. [3] xxiv, 22; Pharm. J. Trans. xiii, 184; Compt. rend. xxxvi, 580.

Brain.—Comparative investigation of the quantities of water and fat in the brain: by *J. Hauff* and *R. Walther*. Ann. Ch. Pharm. lxxxv, 42.

—— On the brain: by *E. v. Bibra*. Ann. Ch. Pharm. lxxxv, 201.

—— On the brain of the new-born infant: by *J. Schlossberger*. Ann. Ch. Pharm. lxxxvi, 119.

Bran.—On the chemical composition of bran: by *M. Poggiale*. Compt. rend. xxxvii, 171; J. Pharm. [3] xxiii, 198.

—— On the influence of the glucosic ferments contained in bran on the process of panification: by *M. Mouriés*. Compt. rend. xxxvii, 427.

—— Report by M. Chevreul on a memoir by M. Mouriés entitled: "On the proximate principles of wheat-bran, of their action in panification, and in the nutrition of animals." Compt. rend. xxxvii, 775.

Brandy.—Means of detecting and separating copper from brandy. Pharm. J. Trans. xiii, 294.

Brass.—Fire-proof bronze-colour for copper and brass: by *M. Dienst*. Chem. Gaz. 1853, 119.

Bread.—Examination of the bread supplied to the troops of the various European powers, and of the chemical composition of bran: by *M. Poggiale*. Compt. rend. xxxvii, 171; J. Pharm. [3] xxiii, 198.

—— Experiments to determine the cause of the difference between new and stale bread: by *M. Boussingault*. Ann. Ch. Phys. [3] xxxvi, 490; Chem. Gaz. 1853, 47.

Bromine.—On a process for determining the equivalents of certain fluid hydrocarbons by means of bromine: by *C. G. Williams*. Chem. Gaz. 1853, 365.

Bronze.—On the alteration of bronzes used for the sheating of the ships. Compt. rend. xxxvii, 131.

Burette.—On a new burette: by *R. Kersting*. Ann. Ch. Pharm. lxxxvii, 33.

Butter.—On butter: by *W. Heintz*. Pogg. Ann. xc, 137.

—— On the composition of butter: by *W. Heintz*. Ber. d. Akad. d. Wiss. zu Berlin, 1853, 303; Chem. Gaz. 1853, 441.

Butyl.—On butylic alcohol: by *A. Wurtz*. Ann. Ch. Pharm. lxxxv, 197.

C.

Cacodyl.—On the cacodyl of valerianic acid: by *W. Gibbs*. Chem. Gaz. 1853, 125.

Cadmium.—On an artificial production of Greenockite, and of some other compounds of cadmium: by *E. Schüler*. Ann. Ch. Pharm. lxxxvii, 34.

Calico-printing.—On the applicability of molybdic acid and the molybdates in dyeing and calico-printing: by *W. H. Kurrer*. Chem. Gaz. 1853, 435.

—— Analysis of a new alloy for the plates for calico-printing. J. pr. Chem. 192; J. Fr. Inst. [3] xxv, 68.

Calluna.—Analysis of the ashes of *Erica carnea* and *Calluna vulgaris Salisb.*, and of the soils on which they grow: by *C. F. Röthe*. Ann. Ch. Pharm. lxxxvii, 118.

Camphor.—On the different kinds of camphor, and on oil of camphor: by *Th. Martius*. J. Pharm. [3] xxiii, 472.

—— On lævocamphoric acid and lævocamphor: by *J. Chautard*. Compt. rend. xxxvii, 166; J. Pharm. [3] xxiii, 168.

Camphors.—Camphor from oil of sassafras. Ann. Ch. Pharm. lxxxvii, 376.

Cantharides.—On the nature of the fat of Cantharides: by *Dr. Gössmann*. Ann. Ch. Pharm. lxxxvi, 317.

Caoutchouc.—On caoutchouc and gutta percha: by *F. C. Calvert*. Pharm. J. Trans. xii, 423.

Caproyl.—On caproic alcohol: by *M. Faget*. Compt. rend. xxxvii, 730.

Capryl.—On caprylic alcohol: by *Wladimir Moschnin*. Ann. Ch. Pharm. lxxxvii, 111.

Carbon.—Observations on carbon and on the difference of temperature of the induced luminous poles: by *M. Despretz*. Compt. rend. xxxvii, 369.

—— On the detection of sulphide of carbon: by *A. Vogel*. Ann. Ch. Pharm. lxxxvi, 369.

Carbonates.—On the occurrence of crystallized carbonate of lanthanum: by *W. O. Blake*. Sill. Am. J. [2] xvi, 228.

—— Improvements in the manufacture of carbonates of soda (W. E. Newton's Patent). Chem. Gaz. 1853, 359.

—— On the preparation of carbonate of potash: by *C. Weber*. Pharm. J. Trans. xiii, 45.

—— On the preparation of carbonate of amyl: by *J. A. Bruce*. Ann. Ch. Pharm. lxxxv, 16.

Casein.—On albumin and casein: by *N. Lieberkühn*. Pogg. Ann. lxxxvi, 117, 298; *abstr.* J. Pharm. [3] xxiii, 398.

Catalysis.—Additional observations on catalytic combustion: by *J. E. Ashby*. Phil. Mag. [4] vi, 77.

Cellulose.—Discovery of a substance in the human body which gives the same reactions as vegetable cellulose: by *M. Virchow*. Compt. rend. xxxvi, 492.

Cement.—Improved cement for resisting fire (Beale's Patent). Pharm. J. Trans. xiii, 234.

Charcoal.—New process for determining the commercial value of animal charcoal: by *M. Corenwinder*. Compt. rend. xxxvii, 610.

—— Memoir on wood-charcoal: by *M. Violette*. Ann. Ch. Phys. [3] xxxix, 291.

—— Second memoir on charcoal: by *M. Violette*. J. Pharm. [3] xxiv, 172.

Chemical Action.—Researches on the quantities of heat disengaged in chemical and molecular actions (3rd, 4th, and 5th parts—Conclusion): by *P. A. Favre* and *J. T. Silbermann*. Ann. Ch. Phys. [3] xxxvii, 406.

—— Note on the chemical compounds produced by *slow action* at the contact of solids and liquids: by *M. Becquerel*. Compt. rend. xxxvi, 209.

—— Considerations on the theory of chemical changes and on the law of equivalent volumes: by *T. S. Hunt*. Sill. Am. J. [2] xv, 226.

Chemical Changes.—Considerations on the theory of chemical changes and on equivalent volumes: by *T. S. Hunt*. Phil. Mag. [4] v, 326.

Chemical Combination.—On the heat of chemical combination: by *T. Woods*. Phil. Mag. [4] v, 10.

Chemical Composition.—New researches on the relations which may exist between crystalline form, chemical composition, and rotatory power: by *L. Pasteur*. Ann Ch. Phys. [3] xxxviii, 437.—Report thereupon: by *H. de Senarmont*. Compt. rend. xxxvi, 757.

Chemical Forces.—On the economical production of mechanical effect from chemical forces: by *J. P. Joule*. Phil. Mag. [4] v, 1.

—— On the mechanical effect of heat and chemical forces: by *W. J. Rankine*. Phil. Mag. [4] v, 6.

Chicory.—On the means of detecting chicory in coffee: by *J. L. Lassaigne*. Pharm. J. Trans. xiii, 224.

Chlorides.—Action exerted by acids and by alkaline and earthy chlorides on oil of turpentine, sugar, alcohol, and wood-spirit: by *M. Berthelot*. Ann. Ch. Phys. [3] xxxviii, 38.

—— Compounds of the sulphides of ethyl and methyl with certain metallic chlorides: by *A. Low*. J. Pharm. [3] xxxv, 251; Ann. Ch. Pharm. lxxxvii, 369; Chem. Gaz. 1853, 361; Compt. rend. xxxvi, 1095.

—— On the analysis of mineral waters containing chloride of magnesium: by *M. Tillmanns*. J. Pharm. [3] xxiii, 234.

Chlorine.—On a new method of determining the amount of available chlorine contained in hypochlorites of lime, potash, or soda: by *A. P. Price*. Chem. Gaz. 1853, 419.

—— Note on the use of chlorine in analyses: by *MM. Rivot, Beudant*, and *Daguin*. Compt. rend. xxxvii, 126; J. Pharm. [3] xxiii, 169.

—— Improvements in the manufacture of chlorine (Pattinson's Patent). Pharm. J. Trans. xii, 354.

Chloroform.—On the nature of the oily substance existing in commercial chloroform: by *H. Pemberton*. Pharm. J. Trans. xii, 599

Chromium.—On the behaviour of certain oxides with caustic potash in the presence of oxide of chromium: by *A. B. Northcote* and *A. H. Church*. Chem. Soc. Qu. J. vi, 54.

—— On minerals accompanying chromic iron: by *T. H. Garret*. Sill. Am. J. [2] xv, 332.

—— On the separation of alumina from oxide of chromium: by *Dexter*. Pogg. Ann. lxxxix, 142.

Chromium.—On the toxicology of bichromate of potash: by *M. Jaillard.* J. Pharm. [5] xxiv, 39.

—— On the combustion of ammonia, &c., by the green oxide of chromium: by *J. E. Ashby.* Phil. Mag. [4] vi, 97.

—— On the preparation of chrome-yellow: by *MM. Riot* and *Delisse,* Pharm. J. Trans. xiii, 139.

—— Cheap method of preparing chrome-red: by *Prof. Runge.* Pharm. J. Trans. xiii, 90.

Cinchona.—Manufacture of chromate and bichromate of potash from chromic iron or chrome ore (J. Booth's Patent). Chem. Gaz. 1853, 478.

—— Researches on the cinchona-alkaloïds: by *L. Pasteur.* Compt. rend. xxxvii, 110; J. Pharm. [3] xxiii, 161; Chem. Soc. Qu. J. vi, 273.

Cinchonine.—Action of carbonic acid on quinine and cinchonine: by *M. Langlois.* Compt. rend. xxxvii, 727.

Citrates.—On the crystalline forms of certain citrates: by *J. C. Heusser.* Pogg. Ann. lxxxviii, 121.

—— On the adulteration of commercial citrate of iron and quinine: by *C. G. Williams.* Chem. Gaz. 1853, 269.

Clay.—Analysis of light-grey clay from Wiesloch: by *J. Moser.* Ann. Ch. Pharm. lxxxv, 99.

—— On plastic clay (*terre molle*): by *M. Barreswil.* J. Pharm. [3] xxii, 444.

Coal.—Description of a brown coal deposit in Brandon, Vermont, U.S.: by *E. Hitchcock.* Sill. Am. J. [2] xv, 95.

—— On the presence of alumina in Bog-head coal, and on the use of the ashes of the latter in the manufacture of alum: by *T. J. Herapath.* Chem. Gaz. 1853, 169.

—— Improved method of treating coal and bituminous substances, and improvements in the treatment of their volatile products (W. Brown's Patent). Chem. Gaz. 1853, 476.

Cobalt.—On an allotropic modification of cobalt: by *F. A. Genth.* Chem. Gaz. 1853, 91.

—— On the new compounds for cobalt described by Frémy and others: by *Prof. Gregory.* Proc. Roy. Soc. Edinb. 1852-53, 193; Ann. Ch. Pharm. lxxxvii, 125.

—— Researches on cobalt: by *E. Frémy.* Ann. Ch. Phys. xxxv, 257; Chem. Gaz. 1853, 201.

—— On a new saline compound of cobalt: by *E. St. Evre.* Ann. Ch. Phys. [3] xxxviii, 177.

—— Cobalt-yellow. Pogg. Ann. lxxxviii, 496.

—— On the compounds of boracic acid and water with protoxide of cobalt: by *H. Rose.* Pogg. Ann. lxxxviii, 299.

—— On the passive state of nickel and cobalt: by *J. Nicklés.* Compt. rend. xxxvii, 284.

—— Separation of nickel from cobalt. Ann. Ch. Pharm. lxxxvii, 128.

—— On the presence of nickel and cobalt in ferruginous waters, and on a process for isolating them: by *O. Henry.* J Pharm. [3] xxiv, 305.

Coca.—On coca leaves: by *H. Wackenroder.* Pharm. J. Trans. xiii, 224.

—— On the properties and composition of the coca-leaf: by *Prof. Johnston.* Chem. Gaz. 1853, 438.

Codeine.—On the rotatory power of codeine: by *Bouchardat* and *F. Boudet*. J. Pharm. [3] xxiii, 288.

Coffee.—On coffee as a beverage, considered in a chemico-physiological point of view: by *J. Lehmann*. Ann. Ch. Pharm. lxxxvii, 205, 275.

—— Examination of the chicoried coffees found in commerce: by *A. Marquis*. J. Pharm. [3] xxiv, 210.

Cohesion.—Memoir on cohesion: by *M. Seguin*. Compt. rend. xxxvii, 698.

Coke.—On the purification of iron and coke from sulphur. J. Fr. Inst. [3] xxv, 47.

Colouring Matter.—On the constitution of the colouring matters of madder: by *E. Schunck*. Phil. Mag. [4] vi, 187.

—— On a new yellow colouring matter in the root-bark of *Rhamnus frangula*: by *L. A. Büchner*. Ann. Ch. Pharm. lxxxvii, 218; J. Pharm. [3] xxiv, 50.

—— Wurrus, a dye from *Rottlera tinctoria*: by *D. Hanbury*. Pharm. J. Trans. xii, 589.

—— Fire-proof bronze-colour for copper and brass: by *M. Dienst*. Chem. Gaz. 1853, 119.

—— Report on English colours: by *E. Ehrmann*. Bull. Soc. Ind. de Mulhouse. No. 115, p. 400.

Copper.—On copper smelting: by *J. Napier*. Phil. Mag. [4] v, 30, 175, 345, 486.

—— On the compounds of boracic acid and water with oxide of copper: by *H. Rose*. Pogg. Ann. lxxxvii, 587.

—— On the chemical compounds of copper and tin, and on mixtures of these metals constituting non-chemical alloys: by *M. Rieffel*. Compt. rend. xxxvii, 450.

—— On the analysis of alloys of copper and zinc: by *H. Spirgatis*. J. pr. Chem. lvii, 84; Chem. Gaz. 1853, 260.

—— Note on sulphantimoniate of copper and zinc: by *Prof. Ettling*. Chem. Soc. Qu. J. vi, 140.

—— On certain compounds of copper with cyanogen: by *A. Dufau*. Compt. rend. xxxvi, 1099.

—— On several new sulphites of cuprous oxide: by *L. Péan de St. Gilles*. J. Pharm. [3] xxiii, 45: Compt. rend. xxxvi, 1086—Remarks thereupon: by *M. Chevreul*. Ibid. 1089.

—— On grey copper (probably a new mineral) from Cabarras County, N. C.: by *F. A. Genth*. Sill. Am. J. [2] xvi, 83.

—— Chloride of zinc as a solvent for copper. Pharm. J. Trans. xiii, 233.

—— On the determination of copper and nickel in quantitative analysis: by *D. Forbes*. Chem. Gaz. 1853, 276.

—— Means of detecting and separating copper in brandy. Pharm. J. Trans. xiii, 294.

—— On the volumetric determination of copper: by *F. Lieshing*. Chem. Gaz. 1853, 472.

Corydalis.—On the occurrence of fumaric acid in *Corydalis bulbosa*: by *W. Wicke*. Ann. Ch. Pharm. lxxxvii, 225.

Cotton.—On the nature of cotton, and on a peculiar fibre of that plant not capable of taking colours: by *W. Crum*. Bull. de la Soc. Industr. de Mulhouse, xxiii, 277.

Cotton.—On the detection of silk, wool, linen, and cotton fibres in textile fabrics: by *G. C. Wittstein.* Pharm. J. Trans. xiii, 181.

—— On the detection of cotton in unbleached linen: by *O. Zimmermann.* Chem. Gaz. 1853, 99.

Crayons.—Crayons for writing on glass: by *R. Brunnquell.* Chem. Gaz. 1853, 193.

Creosote —Contributions to the history of creosote and of some of its products of decomposition: by *Gorup-Besanez.* Ann. Ch. Pharm. lxxxvi, 223.

—— On the behaviour of creosote with lime at a high temperature: by *C. Völckel.* Ann. Ch. Pharm. lxxxvii, 306.

—— On creosote: by *Gorup-Besanez.* Pharm. J. Trans. xiii, 289.

Crystallography.— New researches on the relations which may exist between crystalline form, chemical composition, and rotatory power: by *L. Pasteur.* Ann. Ch. Phys. [3] xxxviii, 437.—Report on the same: by *H. de Senarmont.* Compt. rend. xxxvi, 751.

—— On pseudomorphoses, with consideration of the method of distinguishing certain varieties of them: by *Th. Scheerer.* Pogg. Ann. xc, 315.

—— Chemico-crystallographical investigations: by *C. Rammelsberg.* Pogg. Ann. xc, 12.

—— Researches on the slow formation of crystals at ordinary temperatures: by *M. Lavalle.* Compt. rend. xxxvi, 493.

—— On the production of crystalline structure in crystallized powders by compression and traction: by *D. Brewster.* Trans. Roy. Soc. Edinb. xx, 335; Phil. Mag. [4] vi, 260; *abstr.* Proc. Roy. Soc. Edinb. 1852-53, 578.

—— On circular crystals: by *D. Brewster.* Trans. Roy. Soc. Edinb. xx, 607; *abstr.* Proc. Roy. Soc. Edinb. 1852-53, 188.

—— On the optical phenomena and crystallization of tourmaline, titanium, and quartz, within mica, amethyst, and topaz: by *D. Brewster.* Trans. Roy. Soc. Edinb. xx, 547; Proc. Roy. Soc. Edinb. 1852-53, 158; Phil. Mag. [4] vi, 265.

—— Report on six memoirs by M. Brame on the phenomena which accompany the crystallization of sulphur, phosphorus, and several other bodies: by *M. Dufrénoy.* Compt. rend. xxxvi, 463.

—— On some crystals from the sea-coast of Africa: by *J. Pearsall.* Chem. Gaz. 1853, 418.

Cyanides.—Method of estimating the value of cyanide of mercury: by *F. Lieshing.* J. Pharm. [3] xxiv, 279.

—— On some double salts of cyanide of mercury: by *G. Kohl* and *A. Swoboda.* Chem. Gaz. 1853, 70.

—— On the manufacture of cyanide of potassium by means of atmospheric nitrogen. Pharm. J. Trans. xiii, 291.

Cyanogen.—Analysis of commercial cyanide of potassium: by *MM. Fordos* and *Gélis.* J. Pharm. [3] xxiii, 48.

—— On the use of cyanide of potassium in analytical chemistry: by *H. Rose.* Pogg. Ann. xc, 193.

—— On certain compounds of copper with cyanogen: by *A. Dufau.* Compt. rend. xxxvi, 1099.

Cyanogen.—On the analysis of difficultly decomposible cyanogen-compounds: by *P. Bolley*. Ann. Ch. Pharm. lxxxvii, 254.

—— On the estimation of cyanogen by volume-analysis: by *T. J. Herapath*. Chem. Gaz. 1853, 294.

—— On the preparation of alkaline cyanide for technical purposes: by *R. Wagner*. Pharm. J. Trans. xiii, 141.

—— On the fabrication and valuation of various cyanogen-compounds: by *R. Brunnquell*. Pharm. J. Trans. xiii, 226.

—— On the decomposition of the cyanic ethers: by *A. Wurtz*. Compt. rend. xxxvii, 180.

D.

Didymium.—Researches on didymium and its principal compounds: by *C. Marignac*. Ann. Ch. Phys. [3] xxxviii, 148; Chem. Soc. Qu. J. vi, 260.

Digestion.—New researches on the digestion of amylaceous matters, followed by considerations on digestion in general: by *M. Blondlot*. Compt. rend. xxxvii, 753.

Distillation.—Further examination of the products of the dry distillation of organic bodies: by *C. Völckel*. Ann. Ch. Pharm. lxxxv, 59.

Dyeing.—Chemical researches on dyeing. Ninth memoir: On the action which solid bodies, while they retain the solid state, may exercise on a liquid which holds a solid or a gas in solution: by *M. Chevreul*. Compt. rend. xxxvi, 981.

—— On the introduction of sulphopurpurate of soda (*carmin d'indigo rouge*) into wool and silk dyeing: by *E. Haeffely*. Bull. de la Soc. Industr. de Mulhouse, xxiv, 321.—Report thereupon: by *C. Koechlin*. Ibid. 328.

—— Method of detecting the dyes which have been used in the dyeing of stuffs. Chem. Gaz. 1853, 218.

—— Improvement in the production of the "*Bleu de France*" on wool. J. Fr. Inst. [3] xxv, 69.

—— On the applicability of molybdic acid and the molybdates to dyeing and calico-printing: by *W. H. Kurrer*. Chem. Gaz. 1853, 435.

Dye-stuff.—On a new dye-stuff from China: by *W. Stein*. Chem. Gaz. 1853, 221.

Dye-stuffs.—Importation of Wurrus. Pharm. J. Trans. xiii, 284.

Dye-woods.—Preparation of dye-woods (Brazil's Patent). Chem 1853, 19.

E.

Earths.—On edible earths: by *Dr. Ehrenberg*. J. Pharm. [3] xxiv, 142.

Electricity.—Distribution of electricity on the surface of bodies: by *M. Bourbouze*. Compt. rend. xxxvi, 616.

—— On the law of electrolysis: by *H. Buff*. Ann. Ch. Pharm. lxxxv, 1; Chem. Soc. Qu. J. vi, 47.

—— On some anomalous cases of electrical decomposition: by *W. R. Grove*. Phil. Mag. [4] v, 203.

Electricity.—On the motion of liquids in the closed voltaic circuit: by *G. Wiedemann.* Pogg. Ann. lxxxvii, 321.

—— On silver as a unit of measure for resistance to electric conduction: by *W. Langsdorf.* Ann. Ch. Pharm. lxxxv, 155.

—— Researches on the electric conducting power of gases at high temperatures: by *E. Becquerel.* Compt. rend. xxxvii, 20.

—— On the proper conducting power of liquid-circuits without a metal: by *L. Foucault.* Compt. rend. xxxvii, 580.

—— Note on the calorific effects of the voltaic circuit, considered with regard to the chemical action by which the current is produced: by *P. A. Favre.* Compt. rend. xxxvi, 342.

—— Researches on the conductibility of minerals for voltaic electricity and on the electric light: by *E. Wartmann.* Phil. Mag. [4] v, 12.

—— The electrical relations of iron and copper in solutions at different temperatures: by *G. Gore.* Pharm. J. Trans. xiii, 110.

—— On the position of alloys and amalgams in the thermo-electric series: by *W. Rollmann.* Pogg. Ann. lxxxix, 90.

—— Production of dynamic electricity by the heating and evaporation of liquids: by *M. de Chenot.* Compt. rend. xxxvi, 624.

—— On the electric phenomena attributed to the motion of heat: by *J. M. Gaugain.* Compt. rend. xxxvii, 82.

—— Note on the cause of the development of electricity by rise of temperature: by *M. Leroux.* Compt. rend. [3] xxxvii, 500.

—— On electric phenomena attributed to the motion of heat; in reply to the objections of *M. Leroux*: by *M. Gaugain.* Compt. rend. xxxvii, 653.

—— Researches on thermo-electric currents: by *M. Gaugain.* Compt. rend. xxxvi, 612, 645.

—— Note on the influence of temperature on the electric state of bodies: by *M. Zaliwski.* Compt. rend. xxxvi, 138.

—— On the temperatures of the conductors of electric currents: by *R. Adie.* Phil. Mag. [4] v, 46, 193.

—— On the dependence of galvanic ignition on the nature of the surrounding gas, as observed by Grove: by *R. Clausius.* Pogg. Ann. lxxxvii, 501; Phil. Mag. [4] v, 209.

—— On transient electric currents: by *W. Thomson.* Phil. Mag. [4] v, 393.

—— On certain effects of electric currents: by *A. Masson.* Compt. rend. xxxvi, 1130.

—— On the intensity and quantity of electric currents. Phil. Mag. [4] v, 363.

—— Facts relating to the electric current and the electric light: by *M. Quet.* Compt. rend. xxxv, 949.

—— On a new class of gaseous couples: by *M. Gaugain.* Compt. rend. xxxvii, 584.

—— On electric differences, and on Faraday's sulphide of potassium circuit: by *B. Kohlrausch.* Pogg. Ann. lxxxviii, 464.

—— Substitution of chlorine for oxygen in Bunsen's battery. Reaction which takes place when hydrochloric is substituted for nitric acid in the ordinary battery: by *M. Leroux.* Compt. rend. xxxvii, 588.

Electricity.—On the use of heated sulphuric acid and bioxide of manganese in Bunsen's battery: by *M. Leroux*. Compt. rend. xxxvii, 355.

—— New arrangement of the voltaic battery: by *M. Guignet*. Compt. rend. xxxvii, 174.

—— Cheap method of constructing a galvanic battery: by *W. Symons*. Pharm. J. Trans. xii, 391.

—— Tangent-galvanometer with long wire: by *H. Buff*. Ann. Ch. Pharm. lxxxvi, 1.

—— Description of a new galvanometer, for the absolute measurement of weak as well as of strong currents: by *M. Lamont*. Pogg. Ann. lxxviii, 230.

—— Description of an electroscope with double condenser: by *M. Gaugain*. Compt. rend. xxxvi, 1084.

—— On inductive electrical machines and a means of increasing their effect: by *M. Fizeau*. Compt. rend. xxxvi, 418.

—— On the direction of the induced current produced by the discharge of friction-electricity: by *H. Buff*. Ann. Ch. Pharm. lxxxvi, 293.

—— On the strength of galvanic polarization: by *W. Beetz*. Pogg. Ann. xc, 42.

—— Observations on the electro-chemical properties of hydrogen: by *E. Becquerel*. Ann. Ch. Phys. [3] xxxvii, 385.

—— On the electro-chemical deportment of oxygen: by *M. Kard*. Phil. Mag. [4] vi, 241.

—— An experimental inquiry undertaken with the view of ascertaining whether any and what signs of current force are manifested during the organic process of secretion in living animals: by *H. F. Baxter*. Phil. Trans. 1852, ii, 279.

—— On the solution of urinary calculi in dilute saline fluids at the temperature of the body, by the aid of electricity: by *H. Bence Jones*. Chem. Gaz. 1853, 99.

—— On the reduction and electro-chemical application of tungsten, molybdenum, titanium, and silicium: by *Junot de Bussy*. Compt. rend. xxxvi, 540.

—— Inductive view of electro-metallic deposition: by *G. Gore*. Pharm. J. Trans. xiii, 21.

—— Note on the electric light. Compt. rend. xxxvi, 255.

—— On various electrical phenomena: by *M. Quet*. Compt. rend. xxxvi, 1012.

—— Method of arranging the batteries of Grove, Bunsen, &c., so that they may be always ready for immediate action, and that the substances by whose action the current is produced, may not suffer alteration when the battery is inactive: by *Th. du Moncel*. Compt. rend. xxxvii, 713.

—— Description of a new electrical machine: by *M. Symons*. Pharm. J. Trans. xxxiii, 288.

—— Note on a fact relating to the heating of a conducting wire by the electric current: by *F. de la Provostaye* and *P. Desains*. Compt. rend. xxxvii, 749.

Electrolysis. — On the transference of the irons during electrolysis: by *W. Hittorf*. Pogg. Ann. lxxxix, 177.

Electroplating.—Process for electroplating China-ware. J. Fr. Inst. [3] xxvi, 137.

—— On the recovery of gold and silver from the liquids employed in electroplating and gilding: by *P. Bolley*. Chem. Gaz. 1853, 354; Pharm. J. Trans. xiii, 231.

Endosmose.—On the permeability of porous vessels of inorganic material: by *A. Morin*. J. Pharm. [3] xxiv, 100.

—— Cause of electric endosmose: by *M. Raoult*. Compt. rend. xxxvi, 826.

Equivalent Volumes.—On the constitution and equivalent-volume of some mineral species: by *T. S. Hunt*. Sill. Am. J. [2] xvi, 203.

—— Considerations on the theory of chemical changes, and on the law of equivalent volumes: by *T. S. Hunt*. Sill. Am. J. [2] xv, 226.

Equivalents.—Remarks on certain equivalent numbers: by *R. Schneider*. Pogg. Ann. lxxxviii, 314.

Ergot.—On ergot of rye: by *F. L. Winckler*. Pharm. J. Trans. xiii, 86.

Erica.—Analysis of the ashes of *Erica carnea* and *Calluna vulgaris Salisb.*, and of the soils on which they grow: by *C. F. Röthe*. Ann. Ch. Pharm. lxxxvii, 118.

Ericaceæ.—On the proximate principles contained in the ericaceous family. J. Pharm. [3] xxiii, 476.

—— Chemistry of the plants of the ericaceous family: by *F. Rochleder*. Chem. Gaz. 1853, 189.

Ether.—On the preparation of ether. Pharm. J. Trans. xii, 486.

Ethers.—On ethers intermediate between the œnanthylic, and the methylic, ethylic and amylic series; and on the constitution of castor-oil alcohol by *A. W. Wills*. Chem. Soc. Qu. J. vi. 307.

—— On the decomposition of the cyanic ethers: by *A. Wurtz*. Compt. rend. xxxvii, 180.

Ethyl.—Combinations of the sulphides of ethyl and methyl with certain metallic chlorides: by *A. Loir*. J. Pharm. [3] xxiv, 251; Ann. Ch. Pharm. lxxxvii, 369; Chem. Gaz. 1853, 361; Compt. rend. xxxvii, 1095.

—— Researches on the stannethyls, a series of new organic radicals formed of tin and ethyl: by *C. Löwig*. Ann. Ch. Phys. [3] xxxvii, 343; J. Pharm. [3] xxiii, 234; Chem. Gaz. 1853, 101, 126, 149, 170.

—— On the preparation of crude pelargonate of ethyl: by *R. Wagner*. Chem. Gaz. 1853, 144.

—— On selenide of ethyl: by *C. A. Joy*. Ann. Ch. Pharm. lxxxvi, 35.

—— On some new compounds of tellurethyl: by *Prof. Wöhler*. Chem. Soc. Qu. J. vi, 40; Chem. Gaz. 853, 149.

—— Preparation of ethylamine. Ann. Ch. Pharm. lxxxvi, 374.

—— On a decomposition-product of tetrethylammonium: by *Prof. Weltzien*. Ann. Ch. Pharm. lxxxvi, 292.

Evaporation.—Researches on evaporation: by *Prof. Marcet*. Phil. Mag. [4] vi, 385; Compt. rend. xxxvi, 339.

Explosive Compounds.—Improvements in explosive compounds and fuses for mining and other purposes (Davey and Chance's Patent). Pharm. J. Trans. xii, 354.

Extracts.—Apparatus for the preparation of extracts *in vacuo*: by *MM. Soubeiran* and *Gobley*. J. Pharm. [3] xxiii, 5.

F.

Fats.—On the contractions of glycerine with acids, and on the synthesis of the proximate principles of animal fats: by *M. Berthelot.* Compt. rend. xxxvii, 398; J. Pharm. [3] xxiii, 410; Chem. Soc. Qu. J. vi, 280.

—— Facts relating to the history of fats: by *J. Lefort.* Compt. rend. xxxvii, 28; J. Pharm. [3] xxiii, 113.

—— On the composition of mutton-fat, human fat and spermaceti (Addendum): by *W. Heintz.* Pogg. Ann. lxxxvii, 553.

—— On the composition of beef-suet: by *W. Heintz.* Pogg. Ann. lxxxvii, 579.

—— On Pela or Chinese wax, and on the Chinese vegetable fat called *Fat of Stillirgia:* by *C. Martius.* J. Pharm. [3] xxiv, 224.

—— On the constitution of various fats: by *J. J. Pohl.* Chem. Gaz. 1853, 384.

—— On the nature of the fat of cantharides: by *Dr. Gössmann.* Ann. Ch. Pharm. lxxxvi, 317.

—— Comparative examination of the quantities of water and fat in the brain: by *J. Hauff* and *R. Wagner.* Ann. Ch. Pharm. lxxxv, 42.

—— On the preparation of medicinal oils and fats: by *M. Lhermite.* J. Pharm. [3] xxiv, 349

—— Fat for tempering steel. Rev. Sci. xlii, 396.

Fermentation.—Researches on gallic fermentation: by *C. Robiquet.* J. Pharm. [3] xxiii, 241.

—— Researches on the fermentation of citric acid: by *J. Personne.* Compt. rend. xxxvi, 197.

—— On chemical substitutes for the fermentation of bread. Pharm. J. Trans. xiii, 173.

Ferrocyanides.—On the mutual action of the two ferrocyanides of potassium and of the nitrate and the simple combustion-products of silver: by *O. B. Kühn.* Ann. Ch. Pharm. lxxxvii, 84.

—— On the red colouring of quinine by ferrocyanide of potassium: by *A. Vogel.* Ann. Ch. Pharm. lxxxvi, 122.

Fire.—Cheap red fire. Jahrb. f. pr. Pharm. xxvi, 321; Chem. Gaz. 1853, 385.

Fish.—Some observations on fish in relation to diet: by *J. Davy.* Proc. Roy. Soc. Edinb. 1852-53, 197.

Flax.—On the gases evolved in steeping flax: by *Prof. Hodges.* Chem. Gaz. 1853, 419.

Fluorine.—On the fluorine-salts of antimony: by *F. A. Flückiger.* Chem. Gaz. 1853, 1.

Forensic Chemistry.—On the errors which may be introduced into chemico-legal investigations by the use of charcoal to decolorize liquids containing poisonous substances: by *H. Bonnemains.* Compt. rend. xxxvi, 150. — Remarks on this communication: by *Gaulthier de Claubry.* Ibid. 224.

Fossils.—Chemical investigation of the remains of fossil mammalia: by *F. V. Greene.* Sill. Am. J. [2] xvi, 16.

Frog.—On the constituents of the flesh of the frog: by *Fr. Grohé.* Ann. Ch. Ch. Pharm. lxxxv, 233.

Fuel.—Mode of preparing mineral combustibles so as to give them the same chemical properties as charcoal: by *A. Chenot*. Compt. rend. xxxvi, 152.

Fungi.—On the acids contained in fungi: by *P. Bolley*. Ann. Ch. Pharm. lxxxvi, 44; Chem. Gaz. 1853, 291.

—— On the acids contained in certain fungi: by *M. Dessaignes*. Compt. rend. xxxvii, 782.

Furfurol.—On the preparation of furfurol: by *H. Debus*. Ann. Ch. Pharm. lxxxv, 100.

Fusel-oil.—Examination of the fusel-oil from Indian corn and rye: by *C. M. Wetherill*. Chem. Gaz. 1853, 281; J. Fr. Inst. [3] xxv, 385.

G.

Galls.—Examination of Bassorah galls: by *L. F. Bley*. Arch. Pharm. lxxv, 138; Chem. Gaz. 1853, 468.

Gallstones.—Analysis of gallstones: by *A. v. Planta* and *A. Kekulé*. Ann. Ch. Pharm. lxxxvii, 367.

Gases.—On the Fourth law of the relations of the elastic force, density and temperature of gases: by *R. Potter*. Phil. Mag. [4] vi, 161.

—— Researches on the specific heat of elastic fluids: by *V. Regnault*. Pogg. Ann. lxxxix, 335; Phil. Mag. [4] v, 473.

—— Memoir on the consequences which may be deduced from Regnault's experiments on the law of compressibility of gases: by *M. Avogadro*. Ann. Ch. Phys. [3] xxxix, 140; J. Fr. Inst. [3] xxv, 44.

—— Researches on the electric conducting power of gases at high temperatures: by *E. Becquerel*. Compt. rend. xxxvii, 20.

—— Condensation of gases at the surface of solid bodies: by *J. Jamin* and *A. Bertrand*. Compt. rend. xxxvi, 994; Phil. Mag. [4] vi, 156.

—— On the condensation of gases at the surface of smooth bodies: by *G. Magnus*. Pogg. Ann. lxxxix, 604; Phil. Mag. [4] vi, 334.

—— On an improved apparatus for the analysis of gases: by *E. Frankland* and *W. J. Ward*. Chem. Soc. Qu. J. vi, 197.

—— On the gases evolved in the distillation of sugar: by *C. Völckel*. Ann. Ch. Pharm. lxxxvi, 63.

—— Analysis of gases contained in the soil. Pogg. Ann. lxxxvii, 616.

—— Contributions to the knowledge of the manufacture of gas: by *E. Frankland*. Pharm. J. Trans. xii, 431.

—— Improvements in the purification of coal-gas (Losh's Patent). Pharm. J. Trans. xii, 355.

—— Improvements in the manufacture of coal-gas (Kirkham's Patent). Pharm. J. Trans. xii, 453.

—— Improvements in the manufacture of gas (Vegetable gas) [Booth's Patent]. Pharm. J. Trans. xii, 355.

—— The manufacture of gas from wood or turf: by *J. Ayliffe*. Pharm. J. Trans. xiii, 129.

—— On the use of gas as fuel in organic analysis: by *A. W. Hofmann*. Chem. Soc. Qu. J. vi, 209.

Gases.—New gasometer, serving as a pneumatic trough and as an aspirator: by *M. Tifferau*. Compt. rend. xxxvii, 51.

—— Description of an apparatus for collecting gases over water or mercury: by *W. M. Williams*. Chem. Soc. Qu. J. vi, 44.

Ginger.—On essential oil of ginger: by *A. Papousek*. Pharm. J. Trans. xii, 601.

Glue.—Note on the preparation of liquid glue: by *S. Dumoulin*. Pharm. J. Trans. xii, 392.

Glycerine.—On the compounds of glycerine with acids, and on the synthesis of the proximate principles of animal fats: by *M. Berthelot*. Compt. rend. xxxvii, 398; J. Pharm. [3] xxiii, 410; xxiv, 259; Chem. Soc. Qu. J. vi, 280; Chem. Gaz. 1853, 121.

—— On the preparation of glycerine: by *C. Morfitt*. J. Pharm. [3] xxiv, 357; Pharm. J. Trans. xiii, 84.

—— On the purification of glycerine and its employment in the arts. Pharm. J. Trans. xiii, 137.

Gold.—On the exploitation of gold. Ann. Min. [5] iii, 816, 830.

—— On the situation and working of gold in Australia: by *M. Delesse*. Ann. Min. [5] vi, 179.

—— On the occurrence of gold in Pennsylvania: by *J. W. Mallet*. Phil. Mag. [4] v, 150.

—— On the distribution of gold: by *J. Percy*. Phil. Mag. [4] v, 310.

—— On auriferous quartz: by *A. B. Northcote*. Phil. Mag. [4] vi, 390.

—— Separation of gold from arsenical pyrites, according to Plattner's method: by *W. Guettler*. J. Fr. Inst. [3] xxvi, 180.

—— On the recovery of gold and silver from the liquids employed in electro-plating and gilding: by *P. Bolley*. Chem. Gaz. 1853, 354.

—— Large nugget of gold found in Australia. Pogg. Ann. lxxxviii, 176.

Graduated Solutions.—On improvements in the use of graduated solutions: by *Dr. Mohr*. Ann. Ch. Pharm. lxxxvi, 129.

Grain.—On the value of nutritive grain: by *J. Reiset*. Ann. Ch. Phys. [3] xxxix, 22; Compt. rend. xxxvi, 872.

Granite.—Researches on granite: by *A. Delesse*. Phil. Mag. [4] vi, 206.

Grape-disease.—On the use of pentasulphide of calcium as a means of preventing the grape-disease: by *A. P. Price*. Chem. Gaz. 1853, 414.

Guano.—Examination of guano: by *M. Melsens*.. Chem. Gaz. 1853, 120.

—— The nitre caverns of the Indian Archipelago, a probable source of guano. Pharm. J. Trans. xiii, 136.

—— On commercial guano: by *M. Girardin*. J. Pharm. [3] xxiv, 118.

Guiacum.—Note on extract of guiacum: by *M. Monigaut*. J. Pharm. [3] xxiv, 130.

—— Adulteration of guiacum wood. Pharm. J. Trans. xii, 450.

Gum.—Chemical and pharmacological investigation of gum-kino: by *C. Hennig*. J. Pharm. [3] xxiv, 96.

Gun-barrels.—On the colouring of gun-barrels, and on processes for working on iron and steel. Rev. Sci. xlii, 398.

Gun-cotton.—On the preparation of gun-cotton: by *C. Mann*. Bull. de St. Petersbourg, xi, 210; Pharm. J. Trans. xiii, 71; J. pr. Chem. lix, 141; J. Pharm. [3] xxiv, 371.

Gunpowder.—On a method of determining the quantity of nitrate of potash contained in gunpowder: by *M. Uebatius*. Chem. Gaz. 1853, 433.

Gutta Percha.—On caoutchouc and gutta percha: by *F. C. Calvert*. Pharm. J. Trans. xii, 423.

—— Improvements in the preparation of gutta percha (Rider's Patent). J. Trans. xii, 452.

H.

Heat.—On the mechanical effect of heat and of chemical forces: by *W. J. M. Rankine*. Phil. Mag. [4] v, 6.

—— On the mechanical action of heat: by *W. J. M. Rankine*. Trans. Roy. Soc. Edinb. xx, 591; *abstr.* Proc. Roy. Soc. Edinb. 1852-53, 162.

—— Mechanical theory of heat.—Specific heat of air: by *W. J. M. Rankine*. Phil. Mag. [4] v, 437.

—— Mechanical theory of heat.—Velocity of sound in gases: by *W. J. M. Rankine*. Phil. Mag. [4] v, 483.

—— Observations on heat and its theories: by *A. J. Angström*. Pogg. Ann. lxxxviii, 165.

—— On the elevation and depression of temperature, produced in permanent gases, by compression and dilatation, and by contact with bodies at various temperatures: by *J. H. Koosen*. Pogg. Ann. lxxxix, 437.

—— Hassler's experiments on the expansion of water at various temperatures: by *J. H. Alexander*. Sill. Am. J. [2] xvi, 170.

—— Addition to a memoir entitled "Researches on the relations between the atomic weight and specific heat of elementary bodies": by *M. Granier*. Compt. rend. xxxvii, 130.

—— Researches on the specific heat of elastic fluids: by *V. Regnault*. Pogg. Ann. lxxxix, 335; Phil. Mag. [4] v, 473; Compt. rend. xxxvi, 676.

—— On the specific heat of red phosphorus: by *V. Regnault*. Pogg. Ann. lxxxix, 495; Ann. Ch. Phys. [3] xxxviii, 131.

—— Researches on the quantities of heat disengaged in chemical and molecular actions (3rd, 4th, and 5th parts—Conclusion): by *P. A. Favre* and *J. T. Silbermann*. Ann. Ch. Phys. [3] xxxvii, 406; abstract of the whole series, Chem. Soc. Qu. J. vi, 235.

—— Thermo-chemical researches on compounds formed in multiple proportions: by *P. A. Favre*. J. Pharm. [3] xxiv, 241.

—— On the heat of chemical combination: by *T. Woods*. Phil. Mag. [4] v, 10.

—— On the heat evolved when sulphur-crystals, obtained by fusion, pass into the other form: by *E. Mitscherlich*. Pogg. Ann. lxxxviii, 328.

—— Equilibrium of temperature within envelopes. Researches on the radiating power of rock-salt: by *Provostage* and *Desains*. Compt. rend. xxxvi, 84.

—— Researches on diathermanous bodies: by *M. Melloni*. Compt. rend. xxxvi, 709.

—— Researches on diathermanous substances. Remarks on a communication by MM. de la Provostaye and Desains: by *M. Melloni*. Compt. rend. xxxvii, 590.— Observations on M. Melloni's communication: by *MM. de la Provostaye* and *Desains*. Ibid. 669.

Heat.—Reflection of invisible heat from glass and rock-salt: by *Provostaye* and *Desains*. Compt. rend. xxxvii, 168.—Note on the preceding: by *M. Melloni*. Ibid. 293.

—— Reply to a letter of M. Melloni on the transmission of heat through rock-salt: by *Provostaye* and *Desains*. Compt. rend. xxxvi, 1073.

—— On the heat-conducting power of metals: by *G. Wiedermann* and *R. Franz*. Pogg. Ann. lxxxix, 497.

— Thermic conduction in metals: by *G. Gore*. Phil Mag. [4] vi, 382.

—— On the heat-conduction of metals: by *H. J. Gouillaud*. Pogg. Ann. lxxxviii, 163.

—— Experiments on the relative heat-conducting power of certain rocks: by *G. v. Helmersen*. Pogg. Ann. lxxxviii, 461.

—— Researches on the temperature of the earth at great depths: by *M. Walferdin*. Compt. rend. xxxvi, 250.

—— On the absolute zero of the perfect gas thermometer, being a note to a paper on the mechanical action of heat: by *W. J. M. Rankine*. Trans. Roy. Soc. Edinb. xx, 561; *abstr.* Proc. Roy. Soc. Edinb. 1852-53, 160.

—— Proof of a sensible difference between the mercurial and air-thermometers, from 0° to 100° C.: by *J. Waterston*. Phil. Mag. [4] v, 63.

—— Fundamental principles of a system of thermo-chemistry: by *J. Thomson*. Pogg. Ann. lxxxviii, 349.

—— On the electric phenomena attributed to the motion of heat: by *J. M. Gaugain*. Compt. rend. xxxvii, 82.

—— On the temperatures of the conductors of electric currents: by *R. Adie*. Phil. Mag. [4] v, 46, 209.

—— On the dependence of the heating power of the galvanic current on the nature of the surrounding gas: by *R. Clausius*. Phil. Mag. [4] v, 209.

—— Note on the influence of temperature on the electric state of bodies: by *M. Zaliwski*. Compt. rend. xxxvi, 138.

—— Action of heat on oil of turpentine: by *M. Berthelot*. Ann. Ch. Phys. [3] xxxix, 5.

—— On the precautions to be observed in heating substances in close vessels: by *M. Berthelot*. J. Pharm. [3] xxiii, 357.

—— Temperature at the bottom of the artesian well at Mendorff: by *M. Walferdin*. Pogg. Ann. lxxxix, 349.

Helix.—Analysis of the operculum of the shell of *Helix pomatia*: by *M. Wicke*. Ann. Ch. Pharm. lxxxvii, 221.

Hellebore.—On the occurrence of a crystallizable substance in black hellebore: by *W. Bastick*. Pharm. J. Trans. xii, 174; J. Pharm. [3] xxiv, 159.

Hops.—On oil of hops: by *R. Wagner*. J. pr. Chem. lviii, 6; Chem. Gaz. 1853, 272.

Horn.—On the products of the decomposition of certain horny substances: by *A. C. Leyer* and *Köller*. J. pr. Chem. lviii, 273; Chem. Gaz. 1853, 348.

Humuline.—On the manufacture of humuline. Pharm J. Trans. xiii, 231.

Hydrocarbons.—On a process for ascertaining the equivalents of some fluid hydrocarbons by means of bromine. Chem. Gaz. 1853, 365.

Hydrochlorates.—On hydrochlorate of oil of turpentine: by *M. Berthelot.* Ann Ch. Phys. [3] xxxvii, 223.

Hydrogen.—Observations on the electro-chemical properties of hydrogen: by *E. Becquerel.* Ann. Ch. Phys. [3] xxxvii, 385.

—— On a new oxide of hydrogen, and its relation to ozone: by *M. Baumert.* Pogg. Ann. lxxxix, 37; Phil. Mag. [4] vi, 51; *abstr.* Chem. Soc. Qu. J. vi, 169.

—— On the use of hydrogen in determining vapour-densities, and on the acidification of alcohols by oxygen gas or atmospheric air: by *R. Railton.* Chem. Soc. Qu. J. vi, 205.

—— On the formation of hydrogen and its homologues: by *B. C. Brodie.* Chem. Gaz. 1853, 297.

—— On a modification of hydrogen: by *G. Osann.* J. Pr. Chem. lviii, 385; Chem. Gaz. 1853, 385.

Hygiène.—On certain chemical reactions connected with the hygiène of populous cities: by *M. Chevreul.* Compt. rend. xxxvi, 553.

Hygrometry.—Researches on hygrometry: by *V. Regnault.* Ann. Ch. Phys. [3] xxxvii, 257; Compt. rend. xxxv, 930; Pogg. Ann. lxxxviii, 420.

Hypochlorites.—On a new method of estimating the value of chloride of lime: by *Dr. Penot.* Bull. de la Soc. Ind. de Mulhouse, xxiv, 246; Chem. Gaz. 1853, 217.

—— On a new method for determining the amount of available chlorine in hypochlorites: by *A. P. Price.* Chem. Gaz. 1853, 419.

—— On hypochlorite of magnesia as an antidote to phosphorus: by *M. Bechert.* J. Pharm. [3] xxiv, 352; Pharm. J. Trans. xii, 603.

I.

Incrustation.—Simple means of preventing the formation of incrustations in boilers: by *R. Fresenius.* J. pr. Chem. lviii, 65; Chem. Gaz. 1853, 333.

Indigo.—On the introduction of sulphopurpurate of soda (*carmin d'indigo rouge*) into wool and silk dyeing: by *E. Haeffely.* Bull. de la Soc. Industr. de Mulhouse, xxiv, 321.—Report thereupon: by *C. Koechlin.* Ibid. 328.

—— On the action of soda on the sulphuric compounds of indigo: by *C. Gros-Renaud, Jun.* Bull. de la Soc. Industr. de Mulhouse. xxiv, 343.

—— Process for imparting greater liveliness to indigo-blue in stuffs: by *L. Guillonet.* J. Fr. Inst. [3] xxv, 55.

—— On the determination of the value of commercial indigo: by *E. Wittstein.* Chem. Gaz. 1853, 135; Pharm. J. Trans. xii, 449.

—— On the frequent occurrence of indigo in human urine, and on its chemical and physiological relations: by *A. H. Hassall.* Chem. Gaz. 1853, 355; Pharm J. Trans. xiii, 219.

Ink.—Ink for steel pens: by *F. Runge.* J. Pharm. [3] xxiv, 57.

—— Red ink. Pharm. J. Trans. xii, 601.

Iodides.—On the constitution of iodide of nitrogen: by *R. Bunsen.* Ann. Ch. Pharm. lxxxiv, 1; Ann. Ch. Phys. [3] xxxix, 74; *abstr.* Chem. Soc. Qu. J. vi, 90; J. Pharm. [3] xxiii, 393.

Iodides.—Proto-iodide of tin. Ann. Ch. Pharm. lxxxvi, 374.

Iodine.—On the general distribution of iodine: by *Stevenson Macadam*. Chem. Soc. Qu. J. vi, 166; Pharm. J. Trans. xiii, 178.

—— On the distribution of iodine: by *Prof. Sigwart*. Wurt. Natur. Jahresber. xix, 43; Chem. Gaz. 1853, 228.

—— On the existence of iodine in various plants: by *Stevenson Macadam*. J. Pharm. [3] xxiii, 317.

—— On the pretended occurrence of iodine in milk, eggs, and the atmosphere: by *D. Lohmeyer*. Phil. Mag. [4] vi, 237; Pharm. J. Trans. xiii, 179.

—— Note on the small quantity of iodine contained in the water of the Almendares River (Havannah), and in the land-plants, and the atmosphere of that country: by *M. Casaseca*. Compt. rend. xxxvii, 348.

—— Facts relating to the history of iodine: by *M. Barreswil*. J. Pharm. [3] xxiv, 346.

—— Preliminary notice on a mineral water containing iodine: by *P. Bolley*. Ann. Ch. Pharm. lxxxvi, 51.

—— On the qualitative and quantitative determination of iodine and its separation from bromine and chlorine: by *E. Moride*. Chem. Gaz. 1853, 75.

—— On the determination of iodine: by *R Kersting*. Ann. Ch. Pharm. lxxxvii, 19.

—— On a quick approximative method of estimating minute quantities of iodine: by *T. J. Herapath*. Phil. Mag. [4] vi, 185.

—— On tests for iodine: by *A. Overbeck*. J. Pharm. [3] xxiv, 72; Pharm. J. Trans. xiii, 180.

—— Method of detecting the presence of water in iodine. Pharm. J. Trans. xiii, 181.

—— On the estimation of water in commercial iodine: by *M. Bolley*. Chem. Gaz. 1853, 119.

—— Reproduction of engravings and drawings by means of iodine-vapour: by *Niepcé de St. Victor*. Compt. rend xxxvi, 581.

—— On the iodoquinine compound, investigated in its optical relations by Dr. Herapath and Prof. Stokes: by *W. Haidinger*. Phil. Mag. [4] vi, 273.

—— On the preparation of hydriodate of ammonia. J. Pharm. [3] xxiv, 35.

—— Presence of iodine in rain-water, running water, and in plants from the Antilles and from the coasts of the Mediterranean: by *Ad Chatin*. Compt. rend. xxxvii, 723.

Iridium.—On some new compounds of iridium: by M. *Skohlikoff*. Bull. de St. Petersb. Ch. Phys. Math. Classe xi, 25; Chem. Gaz. 1853, 29.

—— On a probably new element with iridosmine and platinum: by *A. F. Genth*. Sill. Am. J. [2] xv, 246; Chem. Gaz. 1853, 145.

Iron.—Native iron in the Mühlhausen Keuper formation: by *J. G. Bornemann*. Pogg. Ann. lxxxviii, 145, 325.

—— On the meteoric iron of Gütersloh. Pogg. Ann. lxxxvii, 500.

—— Notice of meteoric iron near Lion River, Great Namaqualand, S. Africa, and on the detection of potassium in meteoric iron: by *C. U. Shephard*. Sill. Am. J. [2] xv, 1.

Iron.—Analysis of meteoric iron from Cosby's Creek: by *C. A. Joy*. Ann. Ch. Pharm. lxxxvi, 39.

—— Notice of the meteoric iron found near Seneca River, Cayuga County, N. Y.: by *C. U. Shephard*. Sill. Am. J. [2] xv, 363; Pogg. Ann. lxxxviii, 176.

—— On a new iron-deposit from Obergrund near Zuckmantel: by *E. F. Glocker*. Pogg. Ann. lxxxix, 48.

—— On minerals accompanying chromic iron: by *T. H. Garrett*. Sill. Am. J. [2] xv, 332.

—— On the analysis of cast-iron: by *C. Morfitt* and *J. C. Booth*. Chem. Gaz. 1853, 368, 388, 411; J. Fr. Inst. [3] xxv, 193, 247.

—— Analysis of pig-iron and bog-iron-ore: by *H. L. Buff*. Ann. Ch. Pharm. lxxxiii, 376; Chem. Gaz. 1853, 276.

—— On an iron-ore containing vanadium. Ann. Ch. Pharm. lxxxvi, 127.

—— On the new method employed for the manufacture of iron in the forests of Carinthia: by *M. le Plaq*. Ann. Min. [5] iii, 46.

—— Remarks on the structural conditions of iron: by *T. R. v. Fuchs*. Phil. Mag. [4] v, 389; Chem. Gaz. 1853, 94.

—— On the increased strength of cast-iron produced by the use of improved coke: by *W. Fairbairn*. Chem. Gaz. 1853, 158; J. Fr. Inst. [3] xxv, 375.

—— On the separation of manganese from iron and nickel: by *T. Schiel*. Chem. Gaz. 1853, 413.

—— On the purification of iron and coke from sulphur. J. Fr. Inst. [3] xxv, 47.

—— On the estimation of iron by volume-analysis: by *T. J. Herapath*. Chem. Gaz. 1853, 294.

—— Passive state of nickel and iron: by *J. Nicklès*. Pogg. Ann. xc, 351.

—— On the estimation of protoxide of iron by the method of volumes; by *M. Oppermann*. J. Pharm. [3] xxiii, 294.

—— On the compounds of boracic acid and water with sesquioxide of iron: by *H. Rose*. Pogg. Ann. lxxxix, 473.

—— Action of protosalts of iron on pyroxylin and its congeners: by *M. Béchamp*. Compt. rend. xxxvii, 134.

—— On the impurities in commercial oxide of iron: by *M. Wackenroder*. J. Pharm. [3] xxiii, 240.

—— Comparative experiments with hydrate of magnesia and hydrated sesquioxide of iron as antidotes for arsenic: by *K. D. Schroff*. N. Repert. Pharm. i, 47; J. Pharm. [3] xxiii, 230; Pharm. J. Trans. xiii, 38.

—— Preparation of ammonio-chloride of iron. Pharm. J. Trans. xii, 450.

—— Preparation of lactate of protoxide of iron: by *Thirault de St.-Etienne*. J. Pharm. [3] xxiii, 183.

—— On the adulteration of the citrate of iron and quinine of commerce: by *C. G. Williams*. Chem. Gaz. 1853, 269.

—— On iron and some improvements in its manufacture: by *J. D. Stirling*. J. Fr. Inst. [3] xxvi, 36, 93.

—— Processes for working on iron and steel. Rev. Sci. xlii, 398.

—— Composition for engraving on iron and steel. Rev. Sci. xlii, 405.

—— Syrup of pyrophosphate of iron: by *M. Soubeiran*. J. Pharm. [3] xxiii, 62.

Isomerism.—Contributions to the chemical history of isomeric acids: by *J. Gottlieb.* Ann. Ch. Pharm. lxxxv, 17.

—— On the isomeric modifications of sulphide of antimony. Pogg. Ann. lxxxix, 122.

Isomorphism.—On the isomorphism of Sphene and Euclase: by *J. D. Dana.* Sill. Am. J. [2] xvi, 96.

Ivory.—Improvements in producing ornamental surfaces in metal, ivory, or bone (Skinner's Patent). Chem. Gaz. 1853, 59.

J.

Jalap.—On jalap-root: by *G. Meyer.* Ann. Ch. Phys. [3] xxxvi, 495; J. Pharm. [3] xxii, 463.

K.

Kino.—Chemical and pharmacological examination of kino. Pharm. J. Trans. xxii, 80.

—— On a new source of kino: by *R. Christison.* Pharm. J. Trans. xii, 377.

L.

Lactates.—Preparation of lactate of protoxide of iron: by *Thirault de St.-Etienne.* J. Pharm. [3] xxiii, 183.

—— On the preparation of lactate of protoxide of iron: by *M. Thibault.* Pharm. J. Trans. xiii, 85.

Lakes.—On the preparation of lakes by means of chloride of antimony. Schweiz. Gewerbeblatt xi, 127; Chem. Gaz. 1853, 276.

Lanthanum.—On the occurrence of crystallized carbonate of lanthanum: by *W. P. Blake.* Sill. Am. J. [2] xvi, 228.

Lard.—American lard: by *F. C. Calvert.* Pharm. J. Trans. xii, 388.

Lead.—On tungstate of lead or Scheeletine: by *E. J. Chapman.* Phil. Mag. [4] vi, 120.

—— On the compounds of boracic acid and water with oxide of lead: by *H. Rose.* Pogg. Ann. lxxxvii, 470.

—— On the desilverizing of argentiferous lead by means of zinc: by *Dr. Karsten.* Chem. Gaz. 1853, 132.

Ledum.—On *Ledum palustre*: by *F. Rochleder* and *R. Schwartz.* Chem. Gaz. 1853, 13.

Leucin.—Test for leucin and tyrosin: by *Reinhold Hoffmann.* Ann. Ch. Pharm. lxxxvii, 123.

Light.—On the change of refrangibility of light: by *G. Stokes.* Phil. Trans. 1852, ii, 463.

—— On the chemical action of the solar radiations: by *R. Hunt.* Chem. Gaz. 1853, 415.

—— On the cause of the luminosity of certain bodies when heated: by *Prof. Schrötter.* Chem. Gaz. 1853, 312.

Light.—On the optical phenomena and crystallization of tourmaline, titanium and quartz, within mica, amethyst, and topaz: by *D. Brewster.* Trans. Roy. Soc. Edinb. xx, 547; Phil. Mag. [4] vi, 265; *abstr.* Proc. Roy. Soc. Edinb. 1852-53, 158.

—— Observations, economical and sanitary, on the employment of chemical light for artificial allumination: by *E. Frankland.* J. Fr. Inst. [3] xxvi, 21.

—— On the cause of the luminosity of certain bodies when heated: by *A. Schrötter.* Pharm. J. Trans. xiii, 293.

Lignites.—On peculiar lignites containing wax: by *L. Bruckner.* J. pr. Chem. lvii, 1; J. Pharm. [3] xxiii, 391.

Lime.—Note on the consolidation of stalactites and of calcareous strata: by *M. Fournet.* Compt. rend. xxxvi, 387.

—— On the use of burnt lime instead of limestone as a flux in blast-furnaces: by *E. Montefiore-Levi* and *E. Schmidt.* Chem. Gaz. 1853, 76.

—— New method of determining the value of chloride of lime: by *Dr. Penot.* Bull. de la Soc. Industr. de Mulhouse, 1852, No. 118; Chem. Gaz. 1853, 217.

—— On the effect of sulphate of lime on vegetable substances: by *M. Clausen.* Chem. Gaz. 1843, 437.

Limestone.—Analysis of two limestones: by *A. v. Planta* and *A. Kekulé.* Ann. Ch. Pharm. lxxxvii, 366.

—— On the saccharoïdal limestone of the gneiss of the Vosges: by *M. Delesse.* Bull. de la Soc. Industr. de Mulhouse, xxiv, 55.

Linen.—On the detection of cotton in unbleached linen: by *O. Zimmermann.* Chem. Gaz. 1853, 99.

—— On the detection of silk, wool, linen, and cotton fibres in textile fabrics: by *G. C. Wittstein.* Pharm. J. Trans. xiii, 181.

Liquids.—Phenomena exhibited by certain liquids when thrown in drops on the surface of an ether: by *M. Sire.* Compt. rend. xxxvii, 657.

Lithia.—On the preparation of lithia from triphyline: by *Hugo Müller.* Ann. Ch. Pharm. lxxxv, 251.

Litmus.—Action of carbonic and boracic acid on tincture of litmus: by *J. Malaguti.* Ann. Ch. Phys. [3] xxxvii, 206.

Litter.—Third note on litters and on the effects of lime: by *M. Payen.* Compt. rend. xxxvii, 93.

—— On earthy litter for cattle: by *M. Payen.* Compt. rend. xxxvi, 1017.

—— On marly litter: by *C. Brame.* Compt. rend. xxxvii, 17.

Lucifers.—Manufacture of lucifer matches. J. Fr. Inst. [3] xxvi, 138.

—— On the composition of instantaneous light matches. Pharm. J. Trans. xii, 426.

M.

Madder.—On the constitution of the colouring matters of madder: by *E. Schunck.* Phil. Mag, [4] vi, 187.

—— On madder-root: by *F. Rochleder.* J. pr. Chem. lvi, 85; J. Pharm. [3] xxii, 470.

—— New method of purifying and concentrating the colouring matter of madder (Hughes' Patent). Chem. Gaz. 1853, 380.

Magnesia.—On the preparation of pure magnesia: by *H. Wurtz.* J. Pharm. [3] xxiv, 208.

—— Comparative experiments with hydrate of magnesia and hydrated sesquioxide of iron as antidotes for arsenic: by *K. D. Schroff.* N. Repert. Pharm. i, 47; J. Pharm. [3] xxiii, 230; Pharm. J. Trans. xiii, 38.

—— On hypochlorite of magnesia as an antidote to phosphorus: by *M. Bechert.* J. Pharm. [3] xxiv, 352.

—— Note on the hydrate of chloride of magnesium, melted and in powder: by *M. Casaseca.* Compt. rend. xxxvii, 350.

—— On the analysis of mineral waters containing chloride of magnesium: by *M. Tillmanns.* J. Pharm. [3] xxiii, 234.

Magnetism.—On the action of magnetism on a rectilineally polarized ray in its passage through compressed glass: by *Prof. Edbrund.* Ann. Ch. Pharm. lxxxvii, 338.

Malates.—On the presence of malate of lime in the leaves of the common ash: by *M. Garot.* J. Pharm. [3] xxiv, 308.

Manganese.—On the volumetric determination of manganese-compounds: by *G. Krieger.* Ann. Ch. Pharm. lxxxvii, 257.

—— On a new method for determining the commercial value of oxide of manganese: by *A. P. Price.* Chem. Gaz 1853, 416.

—— On the separation of manganese from nickel and iron: by *T. Schiel.* Chem. Gaz. 1853, 415.

—— Note on the colour exhibited by protosalts of manganese: by *A. Gergen.* Compt. rend. xxxvi, 851.

—— On phosphide of manganese and permanganic acid. Ann. Ch. Pharm. lxxxvi, 371.

—— Preparation of permanganate of potash. Pharm. J. Trans. xiii, 45.

—— Separation of manganese from other metals: by *W. Gibbs.* Ann. Ch. Pharm, lxxxv, 52.

—— On the occurrence of *Manganspath* in Nassau: by *F. Sandberger.* Pogg. Ann. lxxxviii, 491.

—— On the volumetric determination of manganese: by *G. Krieger.* Ann. Ch. Pharm. lxxxvii, 257.

Manure.—Fourth note on various agents for preserving urine and components of the blood for manure: by *M. Payen.* Compt. rend. xxxvii, 473.

—— On the power of soils to absorb manure: by *J. T. Way.* Pharm. J. Trans. xii, 542; xiii, 32.

—— On the influence of iodized manure (marine manure) in preserving the vine from the attacks of the *Oïdium Tuckeri,* and on the peculiar properties of the wine produced by vines thus treated: by *M. Rivet.* Compt. rend. xxxvii, 724.

Membrane.—Observations on the mucous membrane of the intestines: by *Dr. Prevost.* J. Pharm. [3] xxiii, 25.

Membranes.—Experiments on the permeability of membranes by nutritive substances: by *M. Morin.* J. Pharm. xxiii, 10.

Mercury.—On the compounds of the two acids of selenium with the two oxides of mercury, and on native mercurous selenite (Onofrite): by *F. Köhler.* Pogg. Ann. lxxxix, 146.

Mercury.—On several new sulphites of mercuric oxide: by *L. Péan de St. Gilles.* J. Pharm. [3] xxiii, 45; Compt. rend. xxxvi, 1086.—Remarks thereupon: by *M. Chevreul.* Ibid. 1089.

—— On the compounds of basic mercurous nitrate with other nitrates: by *G. Städeler.* Ann. Ch. Pharm. lxxxvii, 129.

—— On the composition of phosphate of mercury: by *R. Brandes.* J. Pharm. [3] xxiv, 80.

—— On selenide of mercury from the Hartz: by *C. Rammelsberg.* Pogg. Ann. lxxviii, 319; Phil. Mag. [4] vi, 272.

—— Method of estimating the value of red cyanide of mercury: by *F. Lieshing.* J. Pharm. [3] xxiv, 272.

—— On some double salts of cyanide of mercury: by *G. Kohl* and *A. Swoboda.* Chem. Gaz. 1853, 70.

—— On Hahnemann's mercurial precipitate. J. Pharm. [3] xxiii, 415.

—— On the permeability of metals to mercury: by *J. Nicklès.* J. Pharm. [3] xxiii, 50; Pogg. Ann. lxxxviii, 335; Chem. Gaz. 1853, 89.

Metals.—On the heat-conduction of metals: by *H. J. Gouillaud.* Pogg. Ann. lxxxviii. 163.

—— On the heat-conducting power of metals: by *G. Wiedemann* and *R. Franz.* Pogg. Ann lxxxix, 497.

—— Thermic conduction in metals: by *G. Gore.* Phil. Mag. [4] vi, 382.

—— Note on the nature of metals: by *M. Tiffereau.* Compt. rend. xxxvii, 579.

—— On some peculiar reduction of metals in the humid way. Ann. Ch. Pharm. lxxxv, 253.

—— On the permeability of metals to mercury: by *J. Nicklès.* Compt. rend. xxxvi, 154; J. Pharm. [3] xxiii, 50; Pogg. Ann. lxxxviii, 335; Chem. Gaz. 1853, 89.

—— On a new series of organic bodies containing metals: by *E. Frankland.* Phil. Trans. 1852, ii, 417; Phil. Mag. [4] v, 159, 239; Ann. Ch. Pharm. lxxxv, 329; *abstr.* Chem. Soc. Qu. J. vi, 57.

—— On the metalliferous veins of Aveyron, and their relation to various products of plutonic action: by *A. Boisse.* Ann. Min. [5] iii, 467.

—— Improved compositions for preventing the oxidation of metals, &c. (Cook's Patent). Pharm. J. Trans. xiii, 234.

—— Improvements in producing ornamental surfaces in metal, ivory, or bone (Skinner's Patent). Chem. Gaz. 1853, 59.

—— Improvements in saline and metallic compounds (Claussen's Patent). Chem. Gaz. 1853, 20.

—— On the principal metallic compositions useful to the armourer. Rev. Sci. xlii, 390.

Meteorite —On the meteoric iron of Gütersloh. Pogg. Ann. lxxxvii, 500.

—— Analysis of meteoric iron from Cosby's Creek: by *C. A. Joy.* Ann. Ch. Pharm. lxxxvi, 39.

—— Nature of the meteoric iron found near Seneca River, Cayuga County, N.Y.: by *C. U. Shephard.* Sill. Am. J. [2] xv, 363.

—— Notice of meteoric iron near Lion River, Great Namaqualand, S. Africa, and on the detection of potassium in meteoric iron: by *C. U. Shephard.* Sill. Am. J. [2] xv, 1.

Meteorite.—On a supposed meteoric stone, alleged to have fallen in Hampshire, in September, 1852: by *G. Wilson.* Proc. Roy. Soc. Edinb. 1852-53, 147.

—— Notice of Prof. Clark's thesis on metallic meteorites. Sill. Am. J. [2] xv, 7.

Methyl.—On the compounds of the sulphides of ethyl and methyl with certain metallic chlorides: by *A. Loir.* J. Pharm. [3] xxiv, 251; Ann. Ch. Pharm. lxxxvii, 369; Chem. Gaz. 1853, 361; Compt. rend. xxxvi, 1095.

—— Researches on stanmethyl, a new organic radical: by *A. Cahours* and *A. Riche.* Compt. rend. xxxvi, 1001.

Methylamine.—On the presence of methylamine on the products accompanying acetone: by *C. G. Williams.* Chem. Gaz. 1853, 409.

Mildew.—On mildew: by *F. C. Calvert.* Pharm. J. Trans. xiii, 283.

Milk.—Facts relating to the chemical history of milk: by *J. Girardin.* [3] xxiii, 401.

—— On the composition of milk: by *MM. Vernois* and *A. Becquerel.* Compt. rend. xxxvi, 187; Chem. Gaz. 1853, 164.

—— On the reaction of fresh milk: by *J. Schlossberger.* Ann. Ch. Pharm. lxxxvii, 317.

—— Note on the presence, in healthy milk, of an albuminoïd principle, which turns the plane of polarization to the left: by *Dovere* and *Poggiale.* Compt. rend. xxxvi, 430.

—— On the presence of albumin in milk in the normal state: by *M. Quévenne.* J. Pharm. [3] xxiv, 94.

—— Note on milk: abnormal secretion of albumin by the mammary gland: by *J. Girardin.* Compt. rend. xxxvi, 753.

—— Remarkable examples of lacteal secretion.—Analysis of the milk in two abnormal cases: by *MM. Joly* and *Filhol.* Compt. rend. xxxvi, 571.

—— On the so-called *Hexenmilch,* a secretion from the mammary glands of new-born infants: by *J. Schlossberger.* Ann. Ch. Pharm. lxxxvii, 324.

—— Note on the estimation of sugar of milk, and on the means of detecting adulterations in milk.

Minerals.—On the classification of minerals: by *E. J. Chapman.* Phil. Mag. [4] vi, 175.

—— On the constitution and equivalent volume of some mineral species: by *T. S. Hunt.* Sill. Am. J. [2] xvi, 203.

—— Artificial formation of minerals: by *N. J. Manross.* Sill. Am. J. [2] xvi, 186.

—— On the formation of crystallized minerals: by *A. Drevermann.* Ann. Ch Pharm. lxxxvii, 126.

—— Researches on the conductibility of minerals for voltaic electricity: by *E. Wartmann.* Phil. Mag. [4] v, 12.

—— New and ready method of determining the alkalis in minerals: by *J. L. Smith.* Part. I. Sill. Am. J. [2] xv, 234; xvi, 53; Chem. Gaz. 1853, 252, 333.

—— Mineralogical notices: On Staurolite, Calcite; on absorption of water by chalk; on Tungstate of Lead or Scheeletine; and on Tinstone pseudomorphs: by *E. J. Chapman.* Phil. Mag. [4] vi, 115.

Minerals.—Contributions to mineralogy: On Tetradymite, Grey Copper, Apophyllite, Allanite, Owenite, Kämmererite (emerald nickel): by *F. A. Genth.* Sill. Am. J. [2] xvi, 81, 167.

—— Re-examination of American minerals: by *J. L. Smith* and *G. J. Brush.* Part. I. Emerylite, Euphyllite, Litchfield Mica, Unionite, Kerolite, Bowenite, Williamsite, Lancasterite, Hydromagnesite, Magnesite: Sill. Am. J. [2] xv, 207.—Part II. Chesterlite, Loxoclase, Danbury Felspars, Haddam Albite, Greenwood Mica, Biotite, Margarodite, Chesterlite Talc, Rhodophyllite, Cummingtonite, Hydrous Anthophyllite, Mourolite, Ozarkite, Dysyntribite, Gibbsite, Emerald Nickels: Sill. Am. J. [2] xvi, 41.

—— Notices of the rarer minerals and new localities in Western North Carolina: Diamond, Gold, Emery, Amethyst, Chalcedonic Quartz, Lazulite, Kyanite, Leopardite: by *C. L. Hunter.* Sill. Am. J. [2] xv, 373.

—— New minerals from Norway. Pt. IV. (Tachyaphalite and Erdmannite): by *N. J. Berlin.* Pogg. Ann. lxxxviii, 160.

—— Chemico-mineralogical researches: by *E. Schmid.*—On the basaltic rocks of the Rhön. Pogg. Ann. lxxxix, 291.

—— On minerals accompanying chromic iron: by *T. H. Garrett.* Sill. Am. J. [2] xv, 332.

Basalt.—On the structure and composition of certain Basaltic and Metamorphic rocks: by *T. Andrews.* Ann. Ch. Pharm. lxxxv, 172; Pogg. Ann. lxxxviii, 321.

.. .. Examination of the basaltic rocks of the Rhön: by *E. Schmid.* Pogg. Ann. lxxxix, 291.

Cerite.—On the composition of Cerite: by *Theodor Kjerulf.* Ann. Ch. Pharm. lxxxvii, 12.

Chiviatite.—On Chiviatite, a new mineral from Peru: by *C. Rammelsberg.* Pogg. Ann. lxxxviii, 320; Phil. Mag. [4] v, 457.

Copper.—On the crystalline form of the Grey Copper of Monzaïa: by *M. Delesse.* Ann. Min. [5] iii, 657.

Dolomite.—Additional observations on the Dolomite of the Franconian Jura, and on the transformation of minerals: by *F. Pfaff.* Pogg. Ann. lxxxvii, 600.

Euclase.—Monograph on Euclase: by *J. Schabus.* Pogg. Ann. lxxxviii, 608.

.. .. Analysis of euclase: by *J. W. Mallet.* Phil. Mag. [4] v, 127.

.. .. On the isomorphism of Sphene and Euclase: by *J. D. Dana.* Sill. Am. J. [2] xvi, 96.

Granite.—On the Granite of the Vosges: by *M. Delesse.* Ann. Min. [5] iii, 369.

Grauwacke.—On the Grauwacke of the Vosges: by *M. Delesse.* Ann. Min. [5] iii, 747.

Greenockite.—On an artificial production of Greenockite, and of some other compounds of Cadmium: by *E. Schüler.* Ann. Ch. Pharm. lxxxvii, 34.

Hayesine.—Analysis of Hayesine: by *A. Deck.* Phil. Mag. [4] vi, 50.

Minerals: Manganese-spar.—On the occurrence of Manganese-spar in Nassau: by *F. Sandberger*. Pogg. Ann. lxxxviii, 491.

Mosandrite.—On the composition of Mosandrite: by *N. J. Berlin*. Pogg. Ann. lxxxviii, 156.

Oligoclase.—Analysis of Oligoclase from the neighbourhood of Wolfach in the Kinzigthal: by *J. Moser*. Ann. Ch. Pharm. lxxxv, 97.

Onofrite.—On native mercurous Selenite (Onofrite): by *F. Köhler*. Pogg. Ann. lxxxix, 146.

Owenite.—On Owenite, a new mineral from the Potomac River: by *F. A. Genth*. Sill. Am. J. [2] xvi, 167.

Phonolite.—Examination of Phonolite from the Rhön: by *E. Schmidt*. Pogg. Ann. lxxxix, 291.

Quartz.—On auriferous Quartz: by *A. B. Northcote*. Phil. Mag. [4] vi, 390.

Realgar.—Insolubility of native Realgar (AsS_2) in carbonate of ammonia: by *C. G. Williams*. Chem. Gaz. 1853, 252.

Romeine.—New researches on the composition of Romeine: by *M. Damour*. Ann. Min. [5] iii, 179.

Sphene.—On the isomorphism of Sphene and Euclase: by *J. D. Dana*. Sill. Am. J. [2] xvi, 96.

Spodumene.—On the composition of North American Spodumene: by *C. Rammelsberg*. Pogg. Ann. lxxxix, 144.

Tellurium.—Analysis of Foliated Tellurium: by *P. H. Schönlein*. Ann. Ch. Pharm. lxxxvi, 201.

Thierschite.—On Thierschite: by *J. Liebig*. Ann. Ch. Pharm. lxxxvi, 113; Chem. Soc. Qu. J. vi, 112.

Tin-pyrites.—On the chemical composition of Tin-pyrites: by *C. Rammelsberg*. Pogg. Ann. lxxxviii, 603.

Topaz.—Account of a remarkable fluid cavity in Topaz: by *D. Brewster*. Phil. Mag. [4] v, 235.

Trachite.—On a metamorphosis of Icelandic Trachyte, whereby it is converted into quartz: by *Th. Kjerulf*. Ann. Ch. Pharm. lxxv, 257.

Trona.—On some supposed crystals of Trona: by *H. J. Brooke*, with an analysis by *A. Dick*. Phil. Mag. [4] v, 373.

Wernerite.—On the composition of Wernerite and its products of decomposition: by *Gerhardt v. Rath*. Pogg. Ann. xc, 62, 288.

Molasses.—On the increase in weight of molasses casks, which occasionally arises from absorption: by *W. Ferguson*. Chem. Soc. Qu. J. vi, 122.

Molecular Action.—Researches in the quantities of heat disengaged in chemical and molecular actions, 3rd, 4th, and 5th parts (conclusion): by *P. A. Favre* and *J. T. Silbermann*. Ann. Ch. Phys. [3] xxxvii, 406.

Molybdenum.—On the reduction and electro-chemical application of molybdenum: by *Junot de Bussy*. Compt. rend. xxxvi, 540.

—— On the applicability of molybdic acid and the molybdates to dyeing and calico-printing: by *W. H. Kurrer*. Chem. Gaz. 1853, 435; Pharm. J. Trans. xiii, 225.

Molybdenum.—On the use of molybdate of ammonia as a test for arsenic in medico-legal inquiries: by *H. Struve.* J. pr. Chem. lviii, 493; J. Pharm. [3] xxiv, 375; Pharm. J. Trans. xiii, 82.

—— Note on a red variety of molybdate of lead from Phœnixville, U.S.: by *C. M. Wetherill.* Phil. Mag. [4] vi, 236.

Mordants.—Improvements in the manufacture of certain mordants used in preparing woven or textile fabrics for printing, staining, or dyeing: (Higgins' Patent). Chem. Gaz. 1853, 440.

N.

Narceine.—On the rotatory power of narceine: by *Bouchardat* and *F. Boudet.* J. Pharm. [3] xxiii, 288.

Nickel.—Note on the presence of nickel and cobalt in certain ferruginous waters, and on a process for isolating them: by *O. Henry.* J. Pharm. [3] xxiv, 305.

—— Separation of nickel from cobalt. Ann. Ch. Pharm. lxxxvii, 128.

—— On the compounds of boracic acid and water with protoxide of nickel: by *H. Rose.* Pogg. Ann. lxxxviii, 361.

—— Analysis of a slag obtained in the smelting of nickel at the Dorothea Works, at Dillenburg: by *W. Winter.* Ann. Ch. Pharm. lxxxvii, 221.

—— Passive state of nickel and iron: by *J. Nicklès.* Pogg. Ann. xc, 351.

—— On the passive state of nickel and cobalt: by *J. Nicklès.* Compt. rend. xxxvii, 284.

—— On the separation of manganese from iron and nickel: by *T. Schiel.* Chem. Gaz. 1853, 413.

—— On the determination of copper and nickel in quantitative analysis: by *D. Forbes.* Chem. Gaz. 1853, 276.

Nitrates.—New test for nitric acid and the nitrates: by *E. W. Davy.* Phil. Mag. [4] v, 330; J. Pharm. [3] xxiv, 206.

—— On the preparation of chemically pure nitrates of potash and soda: by *C. Weber.* Pharm. J. Trans. xii, 596.

—— On a method of determining the quantity of nitrate of potash contained in gunpowder: by *M. Uebatius.* Chem. Gaz. 1853, 433.

—— On the compounds of basic mercurous nitrate with other nitrates: by *G. Städeler.* Ann. Ch. Pharm, lxxxvii, 129.

Nitric Oxide.—On a compound of pelargonic acid with nitric oxide: by *L. Chiozza.* Ann. Ch. Pharm. lxxxv, 225; Chem. Gaz. 1853, 123.

Nitrogen.—On two new methods for the determination of nitrogen in organic and inorganic compounds: by *Maxwell Simpson.* Chem. Soc. Qu. J. vi, 289.

—— New method of forming the protoxide of nitrogen: by *J. L. Smith.* Sill. Am. J. [2] xv, 234; Chem. Gaz. 1853, 250.

—— On nitric acid as a source of the nitrogen found in plants: by *G. Wilson.* Trans. Roy. Soc. Edinb. xx, 591.

—— On the constitution of iodide of nitrogen: by *R. Bunsen.* Ann. Ch. Pharm. lxxxiv, 1; Ann. Ch. Phys. [3] xxxix, 74; *abstr.* Chem. Soc. Qu. J. vi, 90; J. Pharm. [3] xxiii, 393.

Nitroprussides.—On some new methods of forming the nitroprussides: by *E. W. Davy.* Phil. Mag. [4] vi, 11.

Nutrition.—Note on the chemical properties of certain proximate principles of wheat, and their effect in the feeding of animals: by *M. Mouriés.* Compt. rend. xxxvii, 351.

O.

Œnanthyl.—On ethers intermediate between the œnanthylic, and the methylic, ethylic, and amylic series; and on the constitution of castor-oil alcohol: by *A. W. Wills.* Chem. Soc. Qu. J. vi, 307.

Oils.—On a method of distinguishing the volatile oils of the series C_5H_4: by *C. G. Williams.* Phil. Mag. [4] v, 536; J. Pharm. [3] xxiv, 134.

—— Researches on fixed oils of vegetable origin: by *M. Lefort.* J. Pharm. [3] xxiii, 278, 350.

—— On the preparation of medicinal oils and fats: by *M. Lhermite.* J. Pharm. [3] xxiv, 349.

—— Report, presented to the Société de Pharmacie, on a method proposed by M. Behrens for detecting adulteration in oils: by *MM. Guibourt* and *Reveil.* J. Pharm. [3] xxiv, 349.

—— On a method of testing edible oils: by *E. Marchand.* J. Pharm. [3] xxiv, 267.

—— On the analysis of fixed oils by means of sulphuric acid: by *M. Maumené.* Chem. Gaz. 1853, 58; Pharm. J. Trans. xiii, 187.

—— On the fixed vegetable oils of Southern India. Pharm. J. Trans. xii, 598.

—— New process for recognizing the presence of alcohol in essential oils: by *M. Oberdörfer.* J. Pharm. [3] xxiv, 73.

—— On essential oil of bitter almonds: by *D. Maclagan.* Pharm. J. Trans. xiii, 277.

—— Preparation of a drying oil for zinc paint. Pharm. J. Trans. xiii, 294.

—— Means of detecting turpentine in mineral naphtha and in oil of amber: by *Dr. Bolley.* Pharm. J. Trans. xiii, 292.

—— On the compounds of certain volatile oils with the alkaline bisulphites: by *C. Bertagnini.* Ann. Ch. Pharm. lxxxv, 179, 268; Chem. Gaz. 1853, 46.

—— Improvements in preparing oils for lubricating and burning (Hutchison's Patent). Pharm. J. Trans. xii, 551.

—— On the disturbing action exerted by certain metallic salts on drying oils, when exposed to air and light: by *Barruel* and *Jean.* Compt. Rend. xxxvi, 577.

—— On the action of phosphorus on drying oils, chiefly on linseed-oil: by *L. E. Jonas.* Arch. Pharm. [2] lxxx, 139; J. Pharm. [3] xxii, 469.

—— On the volatile oil of beech-tar: by *C. Völckel.* Ann. Ch. Pharm. lxxxvi, 331.

—— Adulteration of oil of cassia with oil of cloves: by *G. Ulex.* Pharm. J. Trans. xii, 602.

—— On oil of camphor: by *Th. Martens.* J. Pharm. [3] xxiii, 473.

—— On cod-liver oil. J. Pharm. [3] xxiii, 426.

—— On the constitution of cod-liver oil. Pharm. J. Trans. xii, 450.

—— Improvements in deodorizing cod-liver oil: by *Sir James Murray.* Pharm. J. Trans. xiii, 188.

—— On the adulteration of olive-oil: by *J. Mackay.* Pharm. J. Trans. xii, 484; also by *Maumené.* Ibid. 497.

—— Solubility of biniodide of mercury in cod-liver oil. Pharm. J. Trans. xiii, 189.

Oils.—On essential oil of coriander. J. Pharm. [3] xxiii, 479; Chem. Gaz. 1853, 16; Pharm. J. Trans. xii, 396.

—— On oil of cummin: by *C. Völckel.* Ann. Ch. Pharm. lxxxv, 246.

—— On volatile oil of ginger: by *M. Papoušk.* J. Pharm. [3] xxiii, 465; Chem. Gaz. 1853, 12; Pharm. J. Trans. xii, 601.

—— On oil of hops: by *R. Wagner.* J. pr. Chem. lviii, 6; Chem. Gaz. 1853, 272.

—— Note on the ozonization of the oils of lemons and turpentine: by *C. G. Williams.* Chem. Gaz. 1853, 331.

—— On the action of ammoniacal bases upon oil of mustard: by *F. Hinterberger.* Chem. Gaz. 1853, 71.

—— On the preparation of oil of morphine: by *M. St. Lager.* J. Pharm. [3] xxiv, 358.

—— Note on the rectification of essential oil of Nerolé: by *M. Danney.* J. Pharm. [3] xxiv, 204.

—— Physiological action of the essential oil of oranges: by *J. Gourbeyre.* Compt. rend. xxxvi, 623.

—— On the acids of rape-oil: by *G. Städeler.* Ann. Ch. Pharm. lxxxvii, 133.

—— Improvements in bleaching palm-oil (Dixon's Patent). Pharm. J. Trans. xiii, 46.

—— Manufacture of resin and of resin-oil. Pharm. J. Trans. xii, 345, 389.

—— On the manufacture of oil of roses. Chem. Gaz. 1853, 98.

—— Camphor from oil of sassafras. Ann. Ch. Pharm. lxxxvii, 376.

—— On essential oil of thyme: by *A. Lallemand.* Compt. rend. xxxvi, 498; J. Pharm. [3] xxiv, 274.

—— Action of heat on oil of turpentine: by *M. Berthelot.* Ann. Ch. Phys. [3] xxxix, 5.

—— On the oil of *Wurmsame:* by *C. Völckel.* Ann. Ch. Pharm. lxxxvii, 312.

Olefiant Gas.—On the production of tar from olefiant gas: by *G. Magnus.* Pogg. Ann. xc, 1; Phil. Mag. [4] vi, 420.

Opium.—On some of the crystalline constituents of opium: by *T. Anderson.* Ann. Ch. Pharm. lxxxvi, 179.

Organic Analysis.—On the use of gas as fuel in organic analysis: by *A. W. Hofmann.* Chem. Soc. Qu. J. vi, 209.

Organic Bases.—Contributions to the history of volatile bases: by *A. Planta* and *A. Kekulé.* Ann. Ch. Pharm. lxxxvii, 1.

Organic Bodies.—On a new series of organic bodies containing metals: by *E. Frankland.* Phil. Trans. 1852, ii, 417; Ann. Ch. Pharm. lxxxv, 329; Phil. Mag. [4] v, 159, 239; *abstr.* J. Pharm. [3] xxiv, 296; Chem. Soc. Qu. J. vi, 57.

Organic Radicals.—Researches on the oxygen-radicals: by *L. Chiozza.* Ann. Ch. Pharm. lxxxiv, 102; Compt. rend. xxxv, 225; Chem. Soc. Qu. J. vi, 182.

—— Researches on stanmethyl, a new organic radical: by *A. Cahours* and *A. Riche.* Compt. Rend. xxxvi, 1001.

Othyl.—Remarks on Professor Williamson's othyl-theory: by *F. Wrightson.* Phil. Mag. [4] vi, 418.

Oxides.—Note on the separation of some metallic oxides: by *M. Flajolot.* Compt. rend. xxxvi, 1090; Chem. Gaz. 1853, 379; Ann. Min. [5] iii, 652.

Oxides.—On the behaviour of certain oxides with caustic potash in the presence of oxide of chromium: by *A. B. Northcote* and *A. H. Church*. Chem. Soc. Qu. J. vi, 54.

Oxygen.—On the electro-chemical deportment of oxygen: by *M. Viard*. Phil. Mag. [4] vi, 241.

—— On the function of oxygen in the life of plants and the action of manure: by *E. Robin*. Rev. Sci xlii, 407.

Ozone.—On a new oxide of hydrogen and its relation to ozone: by *M. Baumert*. Pogg. Ann. lxxxix, 37; Phil. Mag. [4] vi, 51; Chem. Soc. Qu. J. vi, 169.

—— Note on the ozonization of the oils of lemons and turpentine: by *C. G. Williams*. Chem. Gaz. 1853, 331.

P.

Palladium.—Facts relating to the analytical history of palladium and silver: by *A. Béchamp*. J. Pharm. [3] xxiii, 413.

—— On palladamine: by *Hugo Müller*. Ann. Ch Pharm. lxxxvi, 341.

Papaverine.—On the rotatory power of papaverine: by *Bouchardat* and *F. Boudet*. J. Pharm. [3] xxiii, 288.

Papier-maché.—Substitute for papier-maché (Warren's Patent). Chem. Gaz. 1853, 439.

Pelargonates.—On the preparation of crude pelargonate of ethyl: by *R Wagner*. Chem. Gaz. 1853, 144.

Phosphate.—On the composition of phosphate of mercury: by *R. Brandes*. J. Pharm. [3] xxiv, 80.

Phosphates.—Action of caustic potash on the phosphates: by *A. B. Northcote* and *A. H. Church*. Chem. Soc. Qu. J. vi, 53.

Phosphides.—On phosphide of manganese. Ann. Ch. Pharm. lxxxvi, 371.

—— On phosphide of titanium: by *Wöhler*. Ann. Ch. Pharm. lxxxvii, 376.

Phosphorescence.—On the phosphorescence of some marine invertebrata: by *A. de Quatrefages*. Sill. Am. J. [2] xvi, 69.

Phosphorus.—On the specific heat of red phosphorus: by *V. Regnault*. Pogg. Ann. lxxxix, 49; Ann. Ch. Phys. [3] xxxviii, 129.

—— On the discovery of phosphorus: by *J. Ince*. Pharm. J. Trans. xiii, 280.

—— On the so-called amorphous phosphorus: by *A. Puttfarcken*. Ann. Ch. Pharm. lxxv, 136; Chem. Gaz. 1853, 447.

—— Action of phosphorus, sulphur, arsenic, and antimony upon certain classes of salts: by *J. W. Slater*. Chem. Gaz. 1853, 329.

—— On the crystallization of sulphur and phosphorus. Compt. rend. xxxvi, 463.

—— Action of phosphorus on drying oils, chiefly on linseed-oil: by *L. E. Jonas*. Arch. Pharm. [2] lxx, 139; J. Pharm. [3] xxii, 469.

—— On hypochlorite of magnesia as an antidote to phosphorus: by *M. Bechert*. J. Pharm. [3] xxiv, 352; Pharm. J. Trans. xii, 603.

—— Observations on sulphide of phosphorus: by *W. Wicke*. Ann. Ch. Pharm. lxxxvi, 115.

—— Note on the oxide of phosphorus: by *A. Schrötter*. Ann. Ch. Phys. [3] xxxviii, 148.

Photography.—Method of obtaining direct positive photographic impressions on plates of any kind whatever, especially on those which serve for engraving: by *A. Martin*. Compt. rend. xxxvi, 703.

—— New method of obtaining positive impressions, of any dimensions and of equal delicacy with the negative: by *M. Heilmann*. Compt. rend. xxxvii, 136.

—— On the best mode of focussing the photographic apparatus: by *A. Claudet*. J. Fr. Inst. [3] xxvi, 201.

—— On certain causes of failure in photographic operations and on the precautions to be taken to avoid them: by *M. Bertsch*. Compt. rend. xxxvii, 135.

—— On the cause of the occurrence of abnormal figures in photographic impressions of polarized rings: by *G. G. Stokes*. Phil. Mag. [4] vi, 107.

—— Fixation of colours. J. Fr. Inst. [ ] xxv, 141.

—— Process for taking photographic landscapes on paper: by *J. Stewart*. J. Fr. Inst. [3] xxv, 402.

—— On the application of photography to the study of certain phenomena of polarization: by *W. Crookes*. Phil. Mag. [4] vi, 73.

—— Photographic engraving on steel: by *H. F. Talbot*. Compt. rend. xxxvi, 780: also by *M. Niepcé de St. Victor*. Ibid. 908. Remarks on the latter: by *M. Chevreul*. Ibid. 908. Remarks on both memoirs: by *M. Biot*. Ibid. 801.

—— Process for photographic engraving: by *H. F. Talbot*. J. Fr. Inst. [3] xxvi, 121.

—— Application of the microscope to photography: by *W. T. Kingsley*. J. Fr. Inst. [3] xxvi, 188.

—— Photography on stone: by *MM. Barreswil* and *Lemercier*. Chem. Gaz. 1853, 275.

Phycite.—On phycite, the saccharine matter of *Protococcus vulgaris*: by *M. Lamy*. Compt. rend. xxxv, 665. Chem. Gaz. 1853, 200.

Physeline.—On physaline: by *V. Dessaignes* and *J. Chautard*. Chem. Gaz. 1853, 15

Physical Properties.—Observations on certain physical properties of bodies: by *J. Groshans*. Pogg. Ann. Ergänzungsband, iii, 4, 596; further, lxxxviii, 291.

Physiological Chemistry.—On the causes of old age and of death in advanced life: by *E. Robin*. Compt. rend. xxxvi, 147.

Picrotoxine.—On the rotatory power of picrotoxine: by *Bouchardat* and *F. Boudet*. J. Pharm. [3] xxiii, 288.

Piperine.—Researches on a new alkali derived from piperine: by *A. Cahours*. Ann. Ch. Phys. [3] xxxviii, 38; *abstr.* Chem. Soc. Qu. J. vi, 175.

Plants.—On the absorption of inorganic salts by plants: by *Schulz-Fleeth*. Pogg. Ann. lxxxviii, 177.

—— On the existence of iodine in various plants: by *Stevenson Macadam*. J. Pharm. [3] xxiii, 294; Chem. Soc. Qu. J. vi, 168.

Platinum.—On the equivalent weights of platinum and barium: by *T. Andrews*. Ann. Ch. Pharm, lxxxv, 255.

—— On a probably new element associated with iridosmine and platinum: by *A. F. Genth*. Sill. Am. J. [2] xv, 246; Chem. Gaz. 1853, 145.

Poisons.—On the use of *aqua-regia* in testing for poisons: by *Gaultier de Claubry*. J. Pharm. [3] xxiii, 209. Remarks on the same: by *Malaguti* and *Sarzeaud*. Ibid. 296.

—— New mode of analysis for detecting organic poisons: by *C. Flandin*. Compt. rend. xxxvi, 517; Pharm. J. Trans. xiii, 39.

—— Nature of some of the approved processes for the detection of poisons: by *D. Maclagan*. Pharm. J. Trans. xii, 379.

Polarized Light.—New researches on the relations which may exist between crystalline form, chemical composition and rotatory power: by *L. Pasteur*. Ann. Ch. Phys. [3] xxxviii, 437.

—— Report on a memoir by M. Pasteur, entitled "New researches on the relations which may exist between crystalline form, chemical composition and rotatory power": by *H. de Senarmont*. Compt. rend. xxxvi, 757.

—— On the action of magnetism on a rectilineally polarized ray in its passage through compressed glass: by *Prof. Edbrund*. Ann. Ch. Pharm. lxxxvii, 338.

—— Detection of small quantities of soda by means of polarized light: by *Th. Andrews*. Pogg. Ann. lxxxviii, 171.

—— Note on the rotatory powers of quinidine, codeine, narceine, papaverine, and picrotoxine: by *Bouchardat* and *F. Boudet*. J. Pharm. [3] xxiii, 288.

Polymorphism.—Researches on polymorphism: by *J. Nicklès*. J. Pharm. [3] xxiii, 417; xxiv, 5.

Poppy.—Researches on the composition and medicinal properties of the different kinds of white poppy: by *M. Meurien*. J. Pharm. [3] xxiii, 176, 262, 332.

Porcelain.—American porcelain. J. Fr. Inst. [3] xxv, 43.

Porphyry.—On the composition of quartz-porphyry: by *Dr. v. Tribolet*. Ann. Ch. Pharm. lxxxvii, 327.

Potash.—Preparation of pure hydrate of potash: by *Wöhler*. Ann. Ch. Pharm. lxxxvii, 373.

—— On the preparation of carbonate of potash: by *C. Weber*. Pharm. J. Trans. xiii, 43.

—— On the behaviour of certain oxides with caustic potash in presence of oxide of chromium: by *A. B. Northcote* and *A. H. Church*. Chem. Soc. Qu. J. vi, 54.

—— Action of caustic potash on the phosphates: by *A. B. Northcote* and *A. H. Church*. Chem. Soc. Qu. J. vi, 53.

—— On a compound sulphate of potash and soda: by *J. H. Gladstone*. Chem. Soc. Qu. J. vi, 106.

Potassium.—Detection of potassium in meteoric iron: by *C. U. Shepard*. Sill. Am. J. [2] xv, 1.

—— On a new concrete sulphide of potassium: by *M. Gobley*. J. Pharm. [3] xxiii, 350.

Potato.—Remarks on the potato disease: by *T. J. Herapath*. Chem. Gaz. 1853, 362, 382.

Propyl.—On propionic alcohol: by *G. Chancel*. Compt. rend. xxxvii, 410; Chem. Soc. Qu. J. vi, 287.

Protean Stone.—On protean stone, or artificial ivory. J. Pharm. [3] xxii, 444.

Prussiates.—On the mode of estimating the value of red prussiate of potash: by *F. Lieshing*. Chem. Soc. Qu. J. vi, 31; Chem. Gaz. 1853, 139.

Pseudomorphoses.—On pseudomorphoses, with observations on the mode of distinguishing certain kinds of them: by *T. Scheerer*. Pogg. Ann. lxxxix, 1; xc, 315.

Purpurin.—On oxylizaric acid (purpurin): by *H. Debus*. Ann. Ch. Pharm. lxxxvi, 117.

Pyrophosphates.—Syrup of pyrophosphate of iron: by *M. Soubeiran*. J. Pharm. [3] xxiii, 62.

Pyrotartrates.—On pyrotartrate of ammonia, and its transformation by heat: by *A. E. Arppe*. Ann. Ch. Pharm. lxxxvii, 237.

Pyroxyline.—Researches on pyroxyline: by *A. Béchamp*. Ann. Ch. Phys. [3] xxxvii, 206; J. Pharm. [3] xxii, 410.

—— Action of protosalts of iron on pyroxylin and its congeners: by *A. Béchamp*. Compt. rend. xxxvii, 134.

Pressure.—Influence of pressure on the permanence of compounds. Ann. Ch. Pharm. lxxxv, 374.

Q.

Quinidine.—Note on quinidine: by *L. Pasteur*. Compt rend. xxxvi, 26; Chem. Gaz. 1853, 123; J. Pharm. [3] xxiii, 123.

—— Observations on quinidine: by *MM. Bussy* and *Guibourt*. J. Pharm. [3] xxii, 401.

—— On the rotatory power of quinidine: by *Bouchardat* and *F Boudet*. J. Pharm. [3] xxiii, 288.

Quinine.—On the manufacture of large available crystals of sulphate of iodo-quinine (Herapathite) for optical purposes, as artificial tourmalines: by *W. B. Herapath*. Phil. Mag. [4] vi, 346.

—— Action of carbonic acid on quinine and cinchonine; formation of crystallized carbonate of quinine: by *M. Langlois*. Compt. rend. xxxvii, 727.

—— On the *iodo-quinine* examined by Dr. Herapath and Prof. Stokes in its optical relations: by *W. Haidinger*. Pogg. Ann. lxxxix, 250; Phil. Mag. [4] vi, 273.

—— Sulphate of quinine. Pharm. J. Trans. xiii, 209.

—— On the discovery of quinine and quinidine in the urine of patients under medical treatment with the salts of these mixed alkaloïds: by *W. B. Herapath*. Phil. Mag. [4] vi, 171; Pharm. J. Trans. xiii, 216.

—— On the adulteration of the citrate of iron and quinine of commerce: by *C. G. Williams*. Chem. Gaz. 1853, 269.

—— On the red colouring of quinine by ferrocyanide of potassium: by *A. Vogel*. Ann. Ch. Pharm. lxxxvi, 122.

—— Pharmacological researches on tannate of quinine. J. Pharm. [3] xxiii, 158.

R.

Resin.—Manufacture of resin and of resin-oil. Pharm. J. Trans. xii, 345, 389.

—— On a new fossil resin: by *J. W. Mallet*. Ann. Ch. Pharm. lxxxv, 135.

—— On the resin of jalap: by *W. Mayer*. Chem. Gaz. 1853, 21.

Rhamnus.—On rhamnoxanthene, a new yellow colouring-matter, extracted from the root-bark of *Rhamnus frangula*: by *L. A. Buchner*. J. Pharm. [3] xxiv, 50, 293.

Rhododendron.—Examination of the leaves of *Rhododendron ferrugineum*: by *R. Schwartz*. Chem. Gaz. 1853, 44.

Rocks.—Researches on the formation of volcanic rocks in Iceland: by *R. Bunsen*. Ann. Ch. Phys. [3] xxxviii, 215.

—— On the structure and composition of certain basaltic and metamorphic rocks: by *T. Andrews*. Ann. Ch. Pharm. lxxxv, 172; Pogg. Ann. lxxxviii, 321.

—— Researches on the products of the decomposition of rocks by hot sulphurous waters: by *M. Bouis*. Compt. rend. xxxvii, 234.

—— On the theory of the formation of volcanic rocks: by *H. Streng*. Ann. Ch. Phys. xxxix, 52; Pogg. Ann. xc, 103.

—— On the mineralogical and chemical composition of the rocks of the Vosges: by *M. Delesse*. Ann. Min. [5] iii, 369, 747.

Rotten-stone.—On the origin and composition of rotten-stone: by *Prof. Johnston*. Chem. Gaz. 1853, 418; Pharm. J. Trans. xiii, 222.

Rubian.—On rubian and its products of decomposition: by *E. Schunk*. Phil. Mag. [4] v, 410, 495; Ann. Ch. Pharm. lxxxvii, 344.

S.

Saccharometer.—On Soleil's saccharometer: by *W. P. Riddell*. Sill. Am. J. [2] xv, 175.

Sal-ammoniac.—A method of getting rid of sal-ammoniac in analysis: by *J. L. Smith*. Sill. Am. J. [2] xv, 94; Chem. Gaz. 1854, 115.

Salicyl.—On the formation of hydride of salicyl in the flowers of meadow-sweet (*Spirea ulmaria*): by *L. A. Buchner*. J. Pharm. [3] xxiv, 73.

Saline Solutions.—Observations on the supersaturation of saline solutions: by *H. Löwell*. Ann. Ch. Phys. [3] xxxvii, 155, 179.

Saliva.—On the quantitative determination of the sulphocyanide of potassium in saliva: by *T. J. Herapath*. Chem. Gaz. 1853, 294.

Salt.—Note on the probable existence of saliferous strata in the north of France: by *M. Delanoue*. Compt. rend. xxxv, 850.

—— Examination of the *Orber Badesalz*: by *Freiherr v. Bibra*. Ann. Ch. Pharm. lxxxvii, 179.

—— Salt of Western Pennsylvania: by *J. C. Booth* and *T. H. Garrett*. J. Frank. Inst. [3] xxv, 48.

Saltpetre.—Remarks on the artificial productions of saltpetre: by *R. Reichenbach*. Pharm. J. Trans. xiii, 136.

Saltpetre.—Exposition of certain facts relating to the reciprocal action of soluble salt: by *J. Malaguti*. Ann. Ch. Phys. [3] xxxvii, 198; Compt. rend. xxxv, 945.

—— On the relation between the constitution of salts and the quantity of water contained in them: by *P. Kremers*. Pogg. Ann. lxxxviii, 337.

—— On the absorption of inorganic salts by plants: by *Schulz-Fleeth*. Pogg. Ann. lxxxviii, 177.

—— Action of phosphorus, sulphur, arsenic and antimony upon certain classes of salts: by *J. W. Draper*. Chem. Gaz. 1853, 329.

—— Improvements in the manufacture of certain salts of potash, soda, ammonia, lime, and baryta (Price's Patent). Pharm. J. Trans. xiii, 46.

—— Improvements in saline and metallic compounds (Claussen's Patent). Chem. Gaz. 1853, 20.

Sarsaparilla.—On a species of smilax, and a new sort of sarsaparilla obtained from it: by *R. Bentley*. Pharm. J. Trans. xii, 470.

—— On Guatemala sarsaparilla: by *R. Bentley*. J. Pharm. [3] xxiv, 45.

Scammony.—On virgin-scammony and on the characters of scammony-resin: by *W. Ball*. J. Pharm. [3] xxii, 446.

—— Production of scammony in the neighbourhood of Smyrna: by *H. Maltass*. Pharm. J. Trans. xiii, 264.

—— Note on some specimens of scammony: by *D. Hanbury*. Pharm. J. Trans. xiii, 268.

Scilla.—Memoir on *scilla*: by *M. Tilloy*. J. Pharm. [3] xxiii, 406.

Selenium.—On the specific gravity of selenium: by *F. G. Schaffgotsch*. Pogg. Ann. xc, 66.

—— On the compounds of the two acids of selenium with the two oxides of mercury, and on native mercurous selenite (Onofrite): by *F. Köhler*. Pogg. Ann. lxxxix, 146.

—— On selenide of mercury from the Hartz: by *C. Rammelsberg*. Pogg. Ann. lxxxviii, 319; Phil. Mag. [4] vi, 272.

—— On selenide of ethyl: by *C. A. Joy*. Ann. Ch. Pharm. lxxxvi, 35.

Seminaphthalidine.—On azobenzide, azoxybenzide, and seminaphthalidine according to *N. Zinin*. Ann. Ch. Pharm. lxxxv, 328.

Silica.—On the quantitative determination of the alkalis in siliceous minerals not soluble in acids: by *J. L. Smith*. Sill. Am. J. [2] xv, 94; Chem. Gaz. 1853, 252.

—— On deposits of soluble or gelatinous silica in the lower beds of the chalk formation: by *J. T. Way*. Chem. Soc. Qu. J. vi, 102; Pharm. J. Trans. xiii, 174.

—— Analysis of a siliceous deposit from the hot volcanic springs of Taupo, New Zealand: by *J. W. Mallet*. Phil. Mag. [4] v, 285.

Silicium.—On the reduction and electro-chemical application of silicium: by *Junot de Bussy*. Compt. rend. xxxvi, 540.

Silk.—On the detection of silk, wool, linen and cotton fibres and textile fabrics: by *G. C. Wittstein*. Pharm. J. Trans. xiii, 181.

Silver.—On silver as a unit of measure for resistance to electric conduction: by *W. Langsdorf*. Ann. Ch. Pharm. lxxxv, 155.

—— Facts relating to the analytical history of palladium and silver: by *A. Béchamp*. J. Pharm. [3] xxiii, 413.

Silver.—On the compounds of boracic acid and water with oxide of silver: by *H. Rose*. Pogg. Ann. lxxxviii, 482.

—— Hard silver. Pogg. Ann. lxxxviii, 176.

—— On the mutual action between the two ferrocyanides of potassium, and the nitrate and the simple combustion-products of silver: by *O. B. Kühn*. Ann. Ch. Pharm. lxxxvii, 84.

—— On the reactions on which the amalgamation process depends, and on the extraction of silver by amalgamation: by *Dr. Karsten*. Chem. Gaz. 1853, 141.

—— On the desilverizing of argentiferous lead by means of zinc: by *Dr. Karsten*. Chem. Gaz. 1853, 132.

—— Note on a new alloy of silver: by *G. Barruel*. Chem. Gaz. 1852, 15.

—— On the recovery of gold and silver from the liquids employed in electroplating and gilding: by *P. Bolley*. Chem. Gaz. 1853, 354.

Sinapine.—Researches on sinapine: by *L. v. Babo* and *M. Hirschbrunn*. Chem. Gaz. 1853, 81; Chem. Soc. Qu. J. vi, 187; J. Pharm. [3] xxiii, 394; Ann. Ch. Phys. [3] xxxviii, 104.

Soap.—On soaps and their employment in manufactures: by *F. C. Calvert*. Chem. Gaz. 1853, 115.

—— Process for determining the value of soap: by *Dr. Bolley*. Chem. Gaz. 1853, 55.

Soda.—Detection of small quantities of soda by means of polarized light: by *Th. Andrews*. Pogg. Ann. lxxxviii, 171.

—— On the action of soda on the sulphuric compounds of indigo: by *C. Gros-Renaud. Jun.* Bull. de la Soc. Industr. de Mulhouse, xxiv, 343.

—— Improvements in the manufacture of carbonates of soda (W. E. Newton's Patent). Chem. Gaz. 1853, 359.

—— On the presence of soda in commercial potash: by *C. G. Williams*. J. Pharm. [3] xxiv, 290.

—— On a compound sulphate of potash and soda: by *J. H. Gladstone*, Chem. Soc. Qu. J. vi, 106.

—— Notice of a native carbonate of soda found in the territory of Nizam, India: by *W. H. Bradley*. Pharm. J. Trans xii, 515.

Soils.—Analysis of the ashes of *Erica carnea* and *Calluna vulgaris Salisb.*, and of the soils on which they grow: by *C. F. Röthe*. Ann. Ch. Pharm. lxxxvii, 118.

—— Report on a memoir by MM. Verdeil and Rissler, entitled: "Researches on the composition of the soluble matters extracted by water from fertile soils": by *M. de Gasparin*. Compt. rend. xxxvi, 765.

Spermaceti.—On the composition of mutton-fat, human fat, and spermaceti (Addendum): by *W. Heintz*. Pogg. Ann. lxxxvii, 553.

—— Means of powdering spermaceti. Pharm. J. Trans. xii, 550.

Stalactites.—Note on the consolidation of stalactites and of calcareous strata: by *M. Fournet*. Compt. rend. xxxvi, 987.

Stannethyl.—Researches on the stannethyls, a new series of organic radicals formed of ethyl and tin: by *C. Löwig*. Ann. Ch. Phys. [3] xxxvii, 343; *abstr.* J. Pharm. [3] xxiii, 234; Chem. Gaz. 1853, 101, 126, 149, 170.

Stearin.—On the manufacture of stearin candles: by *MM. Lamasse* and *Co.* Bull. de la Soc. Industr. de Mulhouse, xxiii, 314.—Report thereupon: by *Dr. Penot.* Ibid. 317.

Steel.—On the manufacture of cast steel: by *Dr. Karsten.* Chem. Gaz. 1853, 233.

Strychnine.—New method of detecting strychnine and its salts: by *W. Davy.* J. Pharm. [3] xxiv, 204.

—— On the effects of acetate of strychnine (2nd memoir). Compt. rend. xxxvi, 289.

Suet.—On the composition of beef-suet: by *W. Heintz.* Pogg. Ann. lxxxix, 579.

Sugar.—On the processes connected with the manufacture of sugar from beet-molasses. Pharm. J. Trans. xiii, 229.

—— Improvements in refining sugar (Bessemer's Patent). Pharm. J. Trans. xii, 453.

—— Improvements in the manufacture of raw and refined sugar (Brandris' Patent). Pharm. J. Trans. xii, 355.

—— Improvements in the manufacture of sugar (Egan's Patent). Pharm. J. Trans. xii, 453.

—— On MM. Leplay and Dubranfaut's improvements in the manufacture of sugar: by *J. Nicklès.* Chem. Gaz. 1853, 387.

—— Action of alkalis on sugar. Pharm. J. Trans. xii, 348, 393.

—— On the occurrence of aldehyde among the products of the distillation of sugar: by *C. Völckel.* Ann. Ch. Pharm. lxxxvii, 303.

—— On the gases formed in the distillation of sugar: by *C. Völckel.* Ann. Ch. Pharm. lxxxvi, 63.

—— Action exerted by acids and by alkaline and earthy chlorides on sugar: by *M. Berthelot.* Ann. Ch. Phys. [3] xxxviii, 38.

—— On the seat of the sugar formation in the animal body: by *J. Moleschott.* Chem. Gaz. 1853, 381.

—— Note on the estimation of sugar of milk, and on the means of detecting adulterations in milk: by *M. Poggiale.* Compt. rend. xxxvi, 265.

—— Note on the presence of sugar in the urine of epileptic patients: by *Michea* and *Reynoso.* Compt. rend. xxxvi, 230.

Sulphamylates.—Action of ammonia on sulphamylate of lime: by *M. Berthelot.* Ann. Ch. Pharm. lxxxvii, 364; Compt. rend. xxxvi, 1098.

Sulphates.—Process for making sulphate of soda. Pharm. J. Trans. xii, 601.

—— On a compound sulphate of potash and soda: by *J. H. Gladstone.* Chem. Soc. Qu. J. vi, 102; J. Pharm. [3] xxi, 1205.

—— On the preparation of chemically pure sulphate of magnesia: by *C. Weber.* Pharm. J. Trans. xii, 59, 76.

—— On the effect of sulphate of lime on vegetable substances: by *M. Clausen.* Chem. Gaz. 1853, 437.

Sulphides.—Researches on sulphides decomposible by water, followed by general considerations on the production of sulphurous and siliceous waters: by *M. Fremy.* Compt. rend. xxxvi, 178; J. Pharm. [3] xxiii, 161; Ann. Ch. Phys. [3] xxxviii, 312.

—— On the sulphide of antimony: by *Wackenroder.* Arch. Pharm. [2] lxxi, 207; J. Pharm. [3] xxiii, 156.

Sulphides.—On the compounds of the sulphides of ethyl and methyl with certain metallic chlorides: by *A. Lori.* J. Pharm. [3] xxiv, 251; Ann. Ch. Pharm. lxxxvii, 369; Chem. Gaz. 1853, 361; Compt. rend. xxxxi, 1095.

—— On a new concrete sulphide of potassium: by *M. Goble.* J. Pharm. [3] xxiii, 350.

Sulphites.—On several new sulphites of mercuric oxide and cuprous oxide: by *L. Péan de St. Gilles.* J. Pharm. [3] xxiii, 45; Compt. rend. xxxvi, 1086.—Remarks thereupon: by *M. Chevreul.* Ibid. 1089.

—— On the compounds of certain volatile oils with the alkaline bisulphites: by *C. Bertagnini.* Ann. Ch. Pharm. lxxxv, 179, 268; Chem. Gaz. 1853, 46.

Sulphopurpurates.—On the introduction of sulphopurpurate of soda (*carmin d'indigo rouge*) into wool and silk-dyeing: by *E. Haeffely.* Bull. de la Soc. Industr. de Mulhouse, xxiv, 321.—Report thereupon: by *C. Koechlin.* Ibid. 328.

Sulphur.—On the amorphism and polymorphism of sulphur: by *C. Brame.* Compt. rend. xxxvii, 334.

—— On compact transparent sulphur and vitreous arsenious acid: by *C. Brame.* Ann. Ch. Phys. [3] xxxvii, 217.

—— On the heat evolved when crystals of sulphur, obtained by fusion, pass into the other form: by *E. Mitscherlich.* Pogg. Ann. lxxxviii, 328.

—— On the crystallization of sulphur. Compt. rend. xxxvi, 463.

—— On the isomeric compounds of sulphur and antimony: by *H. Rose.* Ber. d. Akad. d. Wiss. zu Berlin, 1853, 242; Chem. Gaz. 1853, 290.

—— Action of sulphur on certain classes of salts: by *J. W. Slater.* Chem. Gaz. 1853, 329.

—— On the purification of iron and coke from sulphur. J. Fr. Inst. [3] xxv, 47.

—— Blue sulphur? Ann. Ch. Pharm. lxxxvi, 373.

—— On the detection of sulphide of carbon: by *A. Vogel.* Ann. Ch. Pharm. lxxxvi, 371.

—— Observations on sulphides of phosphorus: by *W. Wicke.* Ann. Ch. Pharm. lxxxvi, 115.

—— On crystallized sulphur of utricular origin, from Guadaloupe and Vulcano: by *M. Brame.* Compt. rend. xxxvii, 784.

Sulphuretted Hydrogen.—Apparatus for disengaging sulphuretted hydrogen: by *R. Fresenius.* Pharm. J. Trans. xiii, 131.

Syrups.—On syrup of violets: by *F. Kendall.* Pharm. J. Trans. xiii, 18.

—— On syrup of iodide of iron and manganse: by *W. Proctor.* Pharm. J. Trans. xiii, 88.

T.

Tallow.—Purification of tallow and grease. Pharm. J. Trans. xii, 518.

Tangues.—Researches on the *tangues* of Lower Normandy: by *J. I. Pierre.* Ann. Ch. Phys. [3] xxxvii, 81.

Tannates.—Pharmacological researches on tannate of quinine. J. Pharm. [3] xxiii, 158.

Tar.—On the production of tar from olefiant gas: by *G. Magnus*. Pogg. Ann. xc, 1; Phil. Mag. [4] vi, 420.

—— Improvements in the distillation of tar (Shand and M'Clean's Patent). Pharm. J. Trans. xiii, 46.

Tea.—On the adulteration of tea. J. Pharm. [3] xxiv, 228.

Tellurium.—On the action of tellurium on the animal economy: by *K. Hansen*. Ann. Ch. Pharm. lxxxvi, 208.

—— Analysis of foliated tellurinm: by *Ph. Schönlein*. Ann. Ch. Pharm. lxxxvi, 201.

—— On some new compounds of tellurethyl: by *Prof. Wöhler*. Chem. Soc. Qu. J. vi, 40; Chem. Gaz. 1853, 49.

Tetrethylammonium.—On a decomposition-product of tetrethylammonium: by *Prof. Weltzien*. Ann. Ch. Pharm lxxxvi, 292.

Thalia.—On the supposed new element Thalia: by *J. L. Smith*. Sill. Am. J. [2] xvi, 95; Chem. Gaz. 1853, 353.

Thermo-chemistry. — Fundamental principles of a system of thermo-chemistry: by *J. Thomson*. Pogg. Ann. xc, 261.

—— Thermo-chemical researches on combinations formed in multiple proportions: by *P. A. Favre*. J. Pharm. [3] xxiv, 311.

Thermometer.—On the absolute zero of the perfect gas-thermometer; being a note to a paper on the mechanical action of heat: by *W. J. M. Rankine*. Trans. Roy. Soc. Edinb. xx, 561; *abstr.* Proc. Roy. Soc. Edinb. 1852-53, 160.

Thierschite.—Note on Thierschite: by *J. Liebig*. Chem. Soc. Qu. J. vi, 112; Ann. Ph. Pharm. lxxxvi, 113; Ann. Ch. Phys. [3] xxxxiii, 490.

Thorina. — Additional observations on the thorina (oxide of donarium) obtained from Orangite: by *N. J. Berlin*. Pogg. Ann. lxxxvii, 608.

Tin.—Improvements in the manufacture of tin (Michell's Patent). Pharm. J. Trans. xii, 550.

—— Estimation of tin by means of graduated solutions: by *M. St. Léger*. J. Pharm. [3] xxiv, 20.

—— On Tinstone Pseudomorphs: by *E. J. Chapman*. Phil. Mag. [4] vi, 121.

—— On the chemical compounds of copper and tin, and on mixtures of these metals constituting non-chemical alloys: by *M. Rieffel*. Compt. rend. xxxvii, 450.

—— On the chemical composition of tin-pyrites: by *C. Rammelsberg*. Pogg. Ann. lxxxviii, 603.

—— Protiodide of tin. Ann. Ch. Pharm. lxxxvi, 374.

—— Researches on stannethyl: by *A. Cahours* and *A. Riche*. Compt. rend. xxxvi, 1001.

—— Researches on the stannethyls, a series of new organic radicals formed of ethyl and tin: by *C. Löwig*. Ann. Ch. Phys. [3] xxxvii, 343; J. Pharm. [3] xxiii, 234; Chem. Gaz. 1853, 101, 126, 149, 170.

Titanium.—On the reduction and electro-chemical application of titanium: by *Junot de Bussy*. Compt. rend. xxxvi, 540.

—— On phosphide of titanium: by *Wöhler*. Ann. Ch. Pharm. lxxxvii, 375.

Toluidine.—On a new mode of formation of toluidine: by *M. Chautard*. J. Pharm. [3] xxiv, 166.

Toxicology.—On the toxicology of bichromate of potash: by *M. Jaillard*. J. Pharm. [3] xxiv, 38.

Trochus.—Analysis of the operculum of a trohcus: by *W. Wicke.* Ann. Ch. Pharm. lxxxvii, 225.

Tungsten.—On the reduction and electro-chemical application of tungsten: by *Juwot de Bussy.* Compt. rend. xxxvi, 540.

—— On tungstate of lead or Scheeletine: by *E. J. Chapman.* Phil. Mag. [4] vi, 120.

Turpentine.—On the various kind of oils of turpentine: by *M. Berthelot.* Compt. rend. xxxvi, 425.

—— Action of heat on oil of turpentine: by *M. Berthelot.* Ann. Ch. Phys. [3] xxxix, 22.

—— Action of acids and of alkaline and earthy chlorides on oil of turpentine: by *M. Berthelot.* Ann. Ch. Phys. [3] xxxviii, 38.

—— On a product of the action of sulphuric acid on resinized oil of turpentine: by *F. Kuberth.* Chem. Gaz. 1853, 385.

—— On bihydrochlorate of oil of turpentine: by *M. Berthelot.* Ann. Ch. Phys. [3] xxxvii, 223.

Tyrosin.—Test for leucin and tyrosin: by *Reinhold Hoffmann.* Ann. Ch. Pharm. lxxxvii, 123.

U.

Ultramarine.—On commercial ultramarines: by *M. Barreswil.* J. Pharm. [3] xxii, 443.

—— Test of the purity of ultramarine. Pharm. J. Trans. xiii, 40.

Urea.—On some compounds of urea, and on a new method for the determination of chloride of sodium and of urea in urine: by *J. Liebig.* Ann. Ch. Pharm. lxxxv, 289; Chem. Soc. Qu. J. vi, 1; Ann. Ch. Phys. [3] xxxix, 86; J. Pharm. [3] xxiv, 299.

—— Experiments on the production of urea: by *Prof. Bischoff.* Compt. rend. xxxvi, 875; Chem. Gaz. 1853, 289.

—— On a new method for the determination of urea: by *J. W. Draper.* Phil. Mag. [3] vi, 290.

Urine.—Note on the presence of sugar in the urine of epileptic patients: by *Michea* and *Reynoso.* Compt. rend. xxxvi, 230.

—— On the discovery of quinine and quinidine in the urine of patients under medical treatment with the salts of these mixed alkaloids: by *W. B. Heropath.* Phil. Mag. [4] vi, 171.

—— On the frequent occurrence of indigo in human urine, and on its chemical and physiological relations: by *A. H. Hassall.* Chem. Gaz. 1853, 355.

—— On the solution of urinary calculi in dilute saline fluids at the temperature of the body by the aid of electricity: by *H. Bence Jones.* Chem. Gaz. 1853, 99.

V.

Vacuum.—On a method of obtaining a perfect vacuum under the receiver of an air-pump: by *T. Andrews.* Pogg. Ann. lxxxviii, 309.

Vanadium.—On an iron-ore containing vanadium. Ann. Ch. Pharm. lxxxvi, 127.

Vapours.—On the use of hydrogen in determining vapour-densities: by *R. Railton.* Chem. Soc. Qu. J. vi, 205.

Varnishes.—Composition for varnishing iron and steel and protecting them from oxidation. Rev. Sci. xlii, 405.

—— Tinctures and varnishes for the wood-work of fire-arms. Rev. Sci. xlii, 385.

Vegetable Substances.—On the effect of sulphate of lime upon vegetable substances: by *M. Claussen.* Chem. Gaz. 1853, 437.

Vegetation.—Experimental researches on vegetation: by *M. Ville.* Pharm. J. Trans. xii, 489.

Vetch.—Analysis of the ashes of vetch-seed from Neufchatel: by *J. Cohen.* Ann. Ch. Pharm. lxxxv, 288.

Vinegar.—Pyrogallic acid in wood-vinegar. Ann. Ch. Pharm. lxxxvii, 256.

Volcanic Phenomena.—Researches on the intrinsic relations of the pseudo-volcanic phenomena of Iceland: by *R. Bunsen.* Ann. Ch. Phys. [3] xxxviii, 385.

Volcanic Rocks.—On the theory of the formation of volcanic rocks: by *Dr. Streng.* Ann. Ch. Phys. [3] xxxix, 52; Pogg. Ann. xc, 103.

Volumes.—Considerations on the theory of chemical changes, and on equivalent volumes: by *T. S. Hunt.* Phil. Mag. [4] v, 526.

Volumetric Analysis.—On a method of volumetric analysis, of very general application: by *R. Bunsen.* Ann. Ch. Pharm. lxxxvi, 265.

W.

Water.—Hassler's experiments on the expansion of water at various temperatures: by *J. A. Alexander.* Sill. Am. J. xvi, 170.

—— On the influence of water in chemical reactions: by *H. Rose.*

5. On the compounds of boracic acid and water with oxide of lead. Pogg. Ann. lxxxvii, 470.
6. On the compounds of boracic acid and water with oxide of copper. Pogg. Ann. lxxxvii, 587.—Observations in reply to M. Laurent. p. 598.
7, 8, 9. On the compounds of boracic acid and water with protoxide of cobalt, protoxide of nickel and oxide of zinc. Pogg. Ann. lxxxviii, 299.
10. On the compounds of boracic acid and water with oxide of silver. Pogg. Ann. lxxxviii, 482.
11. On the action of boracic acid and water on sesquioxide of iron. Pogg. Ann lxxxix, 473.

—— On the influence of water on boracic acid in borates: by *H. Rose.* Chem. Gaz. 1853, 65.

—— Report on a memoir by A. Reynoso: "On the action of water on various bodies at high temperatures and pressures": by *M. Dumas.* Compt. rend. xxxvi, 411.

—— On the relations between the constitution of salts and the quantity of water contained in them: by *P. Kremers.* Pogg. Ann. lxxxviii, 337.

—— Comparative examination of the quantities of water and fat in the brain: by *J. Hauff* and *R. Wagner.* Ann. Ch. Pharm. lxxxv, 42.

—— Researches on sulphides decomposible by water; followed by general considerations on the production of sulphurous and siliceous waters: by *M. Fremy.* Compt. rend. xxxvi, 178; J. Pharm. [3] xxiii, 161; Ann. Ch. Phys. [3] xxxviii, 312.

Water.—On the estimation of water in commercial iodine: by *M. Bolley*. Chem. Gaz. 1853, 119.

—— Researches on the absorption of atmospheric water by mineral substances: by *M. Durocher*. Compt. rend. xxxvi, 870.

—— Absorption of water by chalk: by *E. J. Chapman*. Phil. Mag. [4] vi, 108.

—— Report on a memoir by MM. Verdeil and Rissler, entitled: "Researches on the composition of the soluble matters extracted by water from fertile soils": by *M. de Gasparin*. Compt. rend. xxxvi, 765.

—— On stagnant waters in general and on "*eaux de mares*" in particular: by *M. Marchand*. Compt. rend. xxxvii, 719.

—— Researches on the products of the decomposition of rocks under the influence of sulphureous thermal waters: by *M. Bouis*. Compt. rend. xxxvii, 234.

—— Note on aerated waters: by *M. Chatin*. J. Pharm. [3] xxiv, 56.

—— On the analysis of rain-water collected and distilled in vessels of platinum: by *M. Barral*. Compt. rend. xxxvi, 184.

—— On the chemical analysis of rain-water: by *M. Martin*. Compt. rend. xxxvi, 487.

—— On the determination of the ammonia contained in waters: by *M. Boussingault*. Compt. rend. xxxvi, 814; Chem. Gaz. 1853, 319.

—— On the quantity of ammonia in rain-water collected at a distance from towns: by *Boussingault*. Compt. rend. xxxvii, 207.

—— Note on the presence of nickel and cobalt in certain ferruginous waters, and on a process for isolating them: by *O. Henry*. J. Pharm. [3] xxiv, 305.

—— Existence of boracic acid in various mineral waters: by *E. Filhol*. Compt. rend. xxxvi, 327; Chem. Gaz. 1853, 113.

—— On the presence of boracic acid in the mineral waters of Wiesbaden and Aix-la-Chapelle: by *Fresenius* and *Wildenstein*. Pharm. J. Trans. xii, 548.

—— On the analysis of mineral waters containing chloride of magnesium: by *M. Tillmanns*. J. Pharm. [3] xxiii, 234.

—— Preliminary notice on mineral water containing iodine: by *P. Bolley*. Ann. Ch. Pharm. lxxxvi, 51.

—— Water from the marshes and subsoil of the *Landes* of Gironde: by *M. Fauré*. Ann. Ch. Phys. [3] xxxix, 83.

—— Chemical examination of the mineral spring at Langenbrücken in the Grand-Duchy of Nassau: by *F. Wandesleben*. Ann. Ch. Pharm. lxxxvii, 248.

—— Note on the presence of the boracic acid in the alkaline sulphureous hot springs of Oletto (Pyrénées Orientales): by *J. Bouis*. Compt. rend. xxxv, 230.

—— On the mineral water of Orezza in Corsica: by *M. Poggiale*. J. Pharm. [3] xxiv, 277.

—— New analysis of the mineral water of Saxon, in the Canton of Valois, Switzerland: by *P. Morin*. J. Pharm. [3] xxiii, 183.

—— Analysis of the sulphur-spring of Serneus: by *A. v. Planta* and *A. Kekulé*. Ann. Ch. Pharm. lxxxvii, 364.

—— Analysis of the Soultzmatt water (Haut-Rhin). Compt. rend. xxxvi, 495.

Water.—Mineral waters of Viterbo: by *M. Poggiale.* J. Pharm. [3] xxiii, 114.
—— Analysis of the waters from the deep wells of Westbourne Park, and Russell Square, and the artesian well of the Hanwell Lunatic Asylum: by *C. H. Clark* and *H. Medlock* Chem. Soc. Qu. J. vi, 115.
—— On the mineral waters of Wiesbaden: by *C. Braun.* J. Pharm. [3] xxiv, 145.
—— Analysis of the Wolkenstein mineral water: by *A. Seyferth.* Ann. Ch. Pharm. lxxxv, 373.
Wax.—On Pela or Chinese wax, and on the Chinese vegetable fat called *Fat of Stillingia*: by *C. Martins.* J. Pharm. [3] xxiv, 224.
—— On the insect white wax of China: by *D. Hanbury.* Pharm. J. Trans. xii, 476; J. Pharm. [3] xxiv, 136.
—— On peculiar lignites containing wax: by *L. Bruckner.* J. pr. Chem. lvii, 1; J. Pharm. [3] xxiii, 391.
—— On the manufacture of wax candles. Pharm. J. Trans. xii, 399.
Wheat.—Note on the chemical properties of certain proximate principles of wheat, and of their effect in the nutrition of animals: by *M. Mouriès.* Compt. rend. xxvii, 351.
Wines.—On the chemical constitution of wines, and on paracitric acid and the paracitrates: by *F. L. Winckler.* Jahrb. f. pr. Pharm. xxv, 65; Chem. Gaz. 1853, 32; J. Pharm. [3] xxiii, 469.
Wood.—Formation of wood by the bark of dicotyledonous trees: by *A. Trécul.* Compt. rend. xxxvi, 138.
—— On the products of the distillation of wood: by *C. Völckel.* Ann. Ch. Pharm. lxxxvi, 66.
Wood-spirit.—Action exerted by acids and by alkaline and earthy chlorides on wood-spirit: by *M. Berthelot.* Ann. Ch. Phys. xxxviii, 38.
Wool.—On the detection of silk, wool, linen, and cotton fibres in textile fabrics: by *G. C. Wittstein.* Pharm. J. Trans. xiii, 181.
Wurrus.—Importation of Wurrus. Pharm. J. Trans. xiii, 284.

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—— Note on amalgamated zinc: by *J. Nicklès.* J. Pharm. [3] xxiii, 124.
—— On the analysis of alloys of copper and zinc: by *H. Spirgatis.* J. pr. Chem. lvii, 84; Chem. Gaz. 1853, 260.
—— Note on sulphantimoniate of copper and zinc: by *Prof. Ettling.* Chem. Soc. Qu. J. vi, 140.
—— On the desilverizing of argentiferous lead by means of zinc: by *Dr. Karsten.* Chem. Gaz. 1853, 132.
—— Chloride of zinc as a solvent for copper. Pharm. J. Trans. xiii, 233.
—— On the compounds of boracic acid and water with oxide of zinc: by *H. Rose.* Pogg. Ann. lxxxviii, 303.
—— Preparation of a drying oil for zinc paint. Pharm. J. Trans. xiii, 294.

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